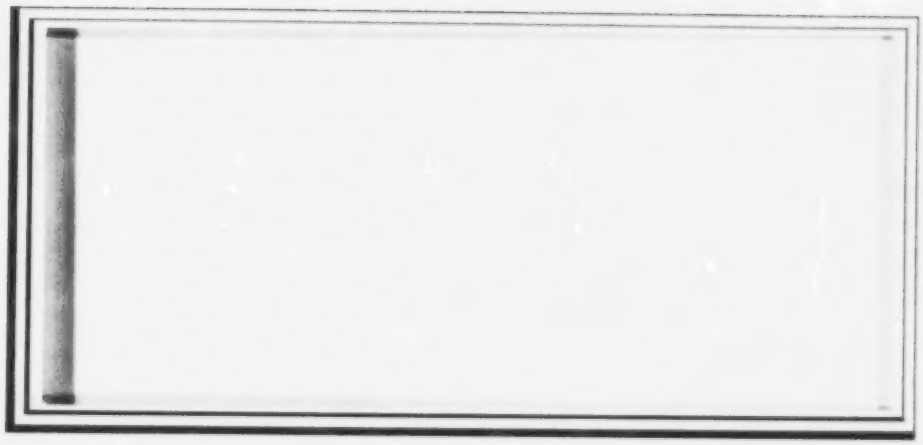

ZENON Environmental Inc.

Evaluation of the Applicability of Reverse Osmosis Technology to Cyanide and Base Metals Recovery From a Gold Mill Barren Bleed, for Economic and Environmental Benefit

FINAL REPORT

BY

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Work on this project was conducted under the auspices of the Mineral Sciences Laboratory, Department of Energy, Mines and Resources

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EMR SCIENTIFIC AUTHORITY: V.M. McNamara

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File No. CO863083

March 3, 1987

Mr. V.M. McNamara
EMR/CANMET
Mineral Sciences Laboratories
555 Booth Street
Ottawa, Ontario
K1A 0G1

Re: **Evaluation of the Applicability of Reverse Osmosis Technology to Cyanide and Base Metals Recovery from a Gold Mill Barren Bleed, for Economic and Environmental Benefit**
DSS File No. 07SQ.23440-5-9203, Contract Serial No. 0SQ85-00309

Dear Mr. McNamara:

We are pleased to submit ten (10) copies of our Final Report on the above referenced project. This final report represents the completion of ZENON's committments under this contract.

As discussed during our telephone conversations, ZENON would be pleased to supply additional engineering input relating to further pilot scale investigations or in the design of a full scale cyanide recovery facility.

We trust this report is satisfactory. If you have any further questions, please contact the undersigned.

Sincerely,

John J. Bancsi

John J. Bancsi, P.Eng.
Project Manager

JJB/mp
Encl.

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EXECUTIVE SUMMARY

CANMET have developed an acidification/volatilization/reneutralization (AVR) process for the recovery of cyanide from gold mill barren bleeds. In order to optimize the AVR process, it is desirable to reduce the volume of wastewater which must be treated by preconcentrating the solution prior to processing. CANMET has determined, based on process characteristics, that reverse osmosis technology may be ideally suited to concentrate the gold mill barren bleeds prior to treatment. The purpose of this study was to examine the feasibility of utilizing commercially available reverse osmosis membranes for this application. Reverse osmosis technology has several characteristics which make it ideally suited to this application. A primary consideration is that when compared to other technologies, reverse osmosis is a very energy efficient concentration process. Also, membranes can potentially provide very high recoveries of cyanides such that the potential exists to produce an environmentally acceptable effluent as a by-product of the concentration. In addition, due to their inherent simplicity, these systems are very easy to operate and are therefore expected to be ideally suited to the mining environment.

This report presents the results of tests carried out with a sample of barren bleed and a sample of barren bleed after acidification and air stripping (AV). Three commercial membranes were evaluated with both waters through "stability" tests. The best performing membrane of the three was subsequently used to concentrate the cyanide.

During the concentration runs, 90% volume reduction was easily achieved with the Toray SP-110 membrane. Cyanide rejections of 90% were obtained with the barren bleed and 70% rejections were achieved with the treated water from the AV process. Thiocyanate rejections were 99% and 84%, respectively. Metals were nearly completly rejected. The permeate flux in the barren bleed was a steady 0.65 $m^3/m^2/d$ (16 U.S.gfd) throughout the concentration test. The permeate flux in the water from the AV process was 1 m^3/m^2-d (25 U.S.gfd) initially and declined to about 0.7 m^3/m^2-d (18 U.S.gfd) with 90% volume reduction.

In these short tests membrane scaling was not observed even though scaling was predicted to occur based on a computer simulation of the concentration runs.

The results produced in this study were used to design and cost a pilot plant for subsequent tests. Pilot plant investigations will be an important next step in the test program to obtain longer term test data on scaling, membrane life, system operation, and maintenance requirements and to further optimize the process design prior to the design of a full scale system.

The pilot plant design which was developed for the next stage of the project work, was scaled up for cost estimating purposes to provide a preliminary estimate of the full scale process economics.

ABRÉGÉ TECHNIQUE

CANMET a mis au point un procédé d'acidification/volatilisation/reneutralisation (AVR) pour la récupération du cyanure des écoulements stériles des usines de traitement de l'or. Afin d'optimiser le procédé AVR, il est souhaitable, avant de commencer, de réduire le volume des eaux usées qui doivent être traitées en concentrant la solution. CANMET a établi qu'en raison des caractéristiques de cette méthode AVR, l'osmose inversée semble la technique idéale pour concentrer les écoulements stériles de traitement de l'or avant d'entamer le traitement AVR. Cette étude a eu pour but d'examiner si les membranes pour osmose inversée du commerce se prêtaient à cette utilisation. La technique de l'osmose inversée présente plusieurs caractéristiques qui en font une méthode convenant idéalement. Un premier atout de l'osmose inversée, comparativement aux autres technologies de concentration, est son faible coût énergétique. Aussi, les membranes ont des taux de récupération de cyanure très élevées qui permettent la production en sous-produit de la concentration d'un effluent acceptable du point de vue environnemental. De plus, en raison de leur simplicité inhérente, ces systèmes sont d'un fonctionnement très facile et donc parfaitement adaptés au milieu minier.

Ce rapport présente les résultats des essais menés avec un échantillon d'écoulement stérile non traité et avec un échantillon traité par acidification et volatilisation (AV). Des essais de "stabilité" ont été menés avec trois membranes du commerce et les deux types d'eaux résiduaires. La meilleure membrane des trois fut celle choisie pour concentrer le cyanure.

Lors des cycles de concentration, il fut aisé d'obtenir une réduction de volume de 90% avec la membrane SP-110 Toray. Avec l'écoulement stérile sans traitement, les rejets de cyanure furent de 90% et avec l'écoulement stérile traité, ils furent de 70%. Les rejets de thiocyanate furent de 99% et 84% respectivement. Les métaux furent presque complètement rejetés. Le taux de filtration au travers de l'écoulement stérile fut en continu de 0,65 m^3/m^2/jour (16 gallons U.S./pi^2/jour) pendant le test de concentration. Le taux de filtration dans les eaux traitées fut de 1 m^3/m^2/jour (25 gallons U.S./pi^2/jour) au départ, et ensuite de 0,7 m^3/m^2/jour (18 gallons U.S./pi^2/jour) avec une réduction de volume de 90%.

Aucun entartrage n'a été observé lors de ces tests de courte durée, alors que d'après une simulation par ordinateur des cycles de concentration, il était prévu qu'il y ait entartrage.

Les résultats de cette étude servirent à concevoir et à chiffrer le coût d'une station pilote devant mener d'autres essais. Les recherches qui seront exécutées dans une telle station représenteront la prochaine étape importante du programme d'essais destiné à obtenir des renseignements à plus long terme sur l'entartrage, la durée de la membrane, le fonctionnement du système et la maintenance nécessaire, et destiné aussi à mieux optimiser la méthode avant de l'appliquer à un système à l'échelle normale.

Le plan de la station pilote mis au point pour la prochaine étape du projet fut ramené aux mesures finales pour fournir une estimation préliminaire des coûts d'une installation d'échelle normale.

1.0 INTRODUCTION

CANMET have developed the Acidification/Volatilization/Reneutralization (AVR) process (McNamara, 1985) for the recovery of cyanide from gold mill barren bleed. In order to improve the cost-effectiveness of the AVR process, it is desirable to reduce the volume of the wastewater which must be treated. Volume reduction can be effected by concentrating the solution prior to processing. Reverse osmosis (RO) has advantages over other volume reduction technologies and these advantages suggest its suitability in this application. For example, the RO process offers high energy efficiency; particularly when compared to evaporation. RO is capable of high recovery efficiencies for complexed cyanides. Furthermore, RO is capable of producing an environmentally acceptable effluent as a by-product of the concentration process. RO is also well suited to automatic operation. Based on these process characteristics, CANMET determined that reverse osmosis technology would be attractive for concentrating gold mill barren bleed prior to treatment by AVR. The purpose of this study was therefore to confirm the expected feasibility of utilizing commercially available RO membranes in this important application.

Recently, a number of non-cellulosic membranes have become available in the commercial marketplace. These membranes greatly extend the acceptable operating range with respect to pH, temperature, and chemical resistance. In addition, these membranes permit the use of a wide range of cleaning agents. Use of these membranes in practice has confirmed claims of reduced fouling and extended membrane life. Moreover, these new membranes have been successfully employed in related applications such as the treatment of plating baths and

rinse waters containing cyanide. These results further suggested the potential for using this technology to treat gold mill barren bleed.

In this study two feedstocks were considered for treatment. The first feedstock was a barren bleed having a pH of 10.9. The second was representative of a feedstock that had passed through the first two steps of the AVR process but had not been reneutralized. The pH of this wastewater was 2.3.

The performance of membranes from three manufacturers was evaluated when applied to the two feedstocks. The membranes selected for evaluation were the following:

High pH Feedstock	Low pH Feedstock
° FT-30*	° FT-30
° Desal-1**	° Desal-2**
° Toray SP-110***	° Toray SP-110

* Filmtec Corp., Minneapolis, MN.

** Desalination Systems Inc., Escondido, CA.

*** Mitsui Corp., New York, N.Y.

The tests carried out included membrane qualification tests as well as stability tests. A concentration test was also conducted but only on the membranes which exhibited superior all-round performance.

The test results were interpreted with respect to the technical and economic suitability of the reverse osmosis process in this application. In addition, recommendations and cost estimates were developed for a pilot scale demonstration at an actual mining site.

2.0 LITERATURE REVIEW

Published information was used to assess the feasibility of applying reverse osmosis technology to gold mill barren bleed for cyanide recovery and pollution control. A computer and manual literature search was undertaken to identify relevant papers but this activity yielded no useful information. Information from membrane manufacturers was reviewed but this yielded only limited information and the collection of publications from in-house sources yielded limited information as well.

All of the papers which were reviewed document the successful application of RO technology to metal finishing operations. While metal finishing rinse waters are somewhat different from the gold mine barren bleed the suitability of RO treatment can be inferred (McNamara[4]).

With an FT-30 membrane, Larson et al[3] observed rejections for free CN^- ranging between 91% and 99%; rejections for $Cu(CN)_4^{2-}$ in excess of 99%; and rejections for $Zn(CN)_4^{2-}$ ranging between 98% and 99%. These tests were run with wastewater having a pH ranging between 9 and 13. No further operating, membrane stability or membrane fouling information was stated.

Spatz[6] reported on tests which showed CN^- rejections of 90% to 95% and $Fe(CN)_6^{-3}$ rejections in excess of 99%. The CN^- rejection was found to be highly pH dependent.

Golomb[2] reported rejections of CN^- ranging between 92% and 99%, and rejections of Zn^{++} and Cu^{++} in excess of 98% and 99% respectively from electroplating wastewater using a Dupont B-9 hollow fiber permeator operated at 400 psig.

While none of the authors provided any data on membrane fouling and long term stability, they cautioned potential users to evaluate each application and supply pretreatment as necessary.

In general our review of the published literature confirmed the suggestion that reverse osmosis can be used successfully to concentrate cyanide in gold mill barren bleed solutions for recovery and pollution control. Membrane stability and fouling were not addressed in the literature and these aspects remain to be determined.

3.0 EXPERIMENTAL

3.1 Test Equipment

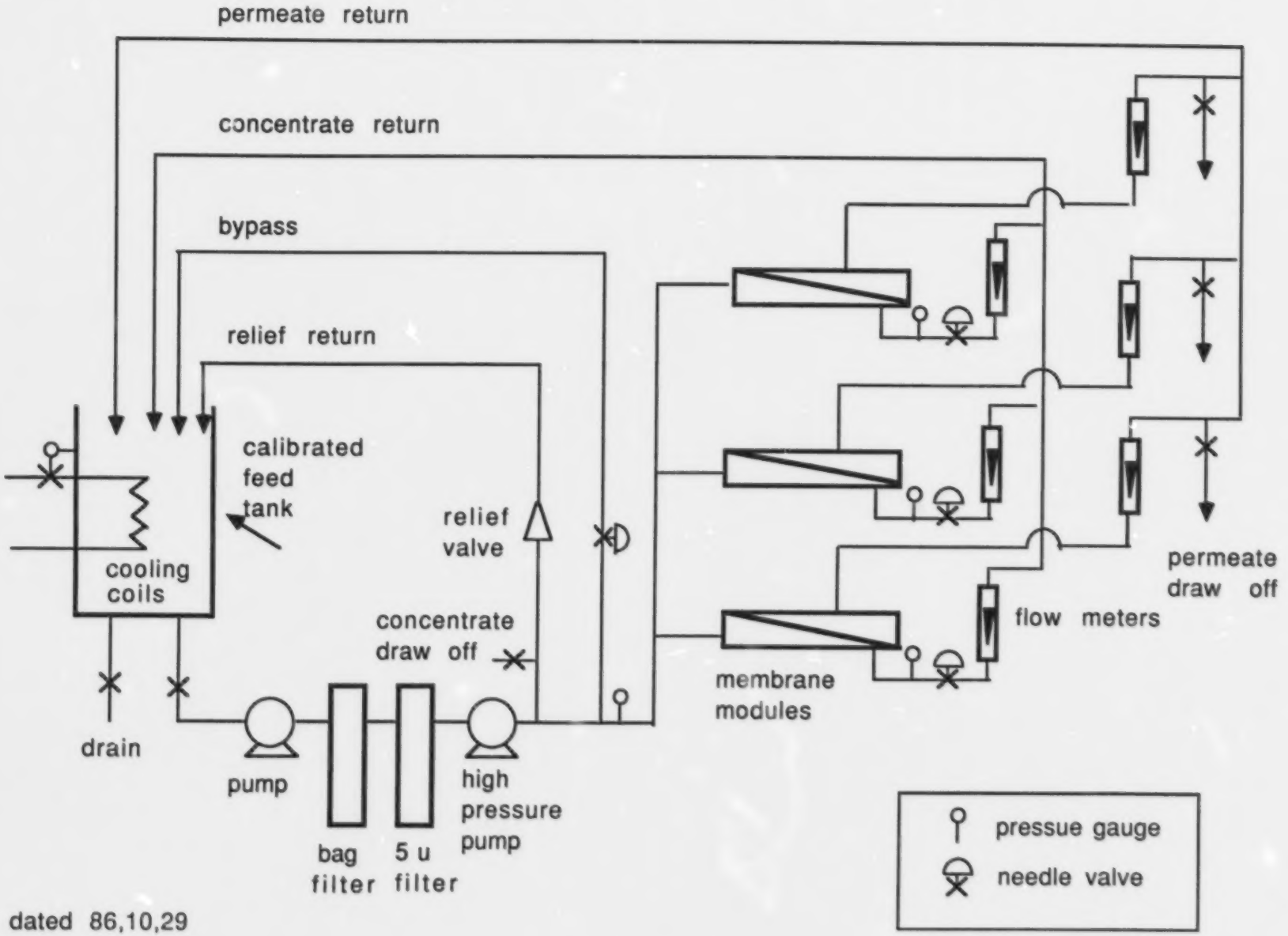
3.1.1 Membrane Selection Test System

The test unit, illustrated in Figure 3-1, was designed to operate with three 10 cm x 100 cm (4" x 40") spiral membrane modules arranged in parallel and fed from a common source. Provision was also made to run up to 6 modules in a cascading mode.

The major components of the test system are the following:

- diaphram process pump rated 76 L/min (20 gpm) @ 6900 kPa (1000 psig), (Model D-25, Wanner Engineering, Minneapolis, MN)
- seal-less magnetic drive feed pump rated at 132 L/min (35 USGPM) @ 137 kPa (20 psig), (Model TE-6T-MD March Manufacturing Co.)
- two - 91 cm (20 inch) polypropylene filter housings; with the lead housing containing a 5 micron polyester filter bag and the lag housing containing a 5 micron polyester filter cartridge
- needle valves and relief valve, (Swagelok)
- pressure gauges rated to 6900 kPa (1000 psig)
- rotameter type flowmeter
- low pressure shut-off switch
- 200 L (44 igal) feed tank
- 200 L (44 igal) rinse tank
- temperature control system in the feed tank (Danfoss Mfg. Co. Ltd., Mississauga, Ont.)

FIGURE 3 - 1. TEST SYSTEM FOR MEMBRANE SELECTION RUNS



On the high pressure side of the system, 316 stainless steel components were used. On the low pressure side of the system components were made of polypropylene, polyethylene, acrylic, and PVC.

Under normal operating conditions, the feed pump moves the feed stock through the filters to the process pump. Since the feed to the process pump must be supplied at pressure in order to preclude pump damage arising from starvation, upstream protection for the process pump is provided in the form of a low pressure shut off switch. The process pump pressurizes and moves the liquid through the membrane modules.

Pressures and flowrates through the modules may be regulated by adjustment of the needle valves at the outlet of each module. Since there is a relationship between flowrate and pressure, all four valves require adjustment in order to obtain the desired hydraulic conditions. The flow of liquid, in excess of that passing through the modules, is returned to the feed tank through a bypass line. Flow in this line is valve-controlled. A pressure relief valve also permits the return of liquid back to the feed tank in the event of a system blockage.

The measurement of both permeate and concentrate flowrate is facilitated by the provision of flowmeters downstream of the modules. Provision for sampling each stream is also made.

The test system includes temperature control of the feed tank through cooling in order to permit the maintenance of the feed temperature at a set level during recirculation.

In addition, a wash/rinse tank is provided in this system to minimize the cyanide discharge during the membrane cleaning process.

3.1.2 Concentration Test System

The test system used for the concentration runs is shown in Figure 3-2. This equipment is similar to that shown in Figure 3-1. However, there were some modifications. Only one membrane module was used and the permeate could be either returned to the feed tank or directed into a container for subsequent discharge.

3.1.3 Test Area

A movable enclosure was constructed to house the test equipment. The enclosure structure comprised a 2 x 4 frame lined with heavy gauge polyethylene sheeting. Provisions were included to contain and to decontaminate spills. The ventillation system for the enclosure provides for 8 air changes a minute. Exhaust is to the external ambient atmosphere.

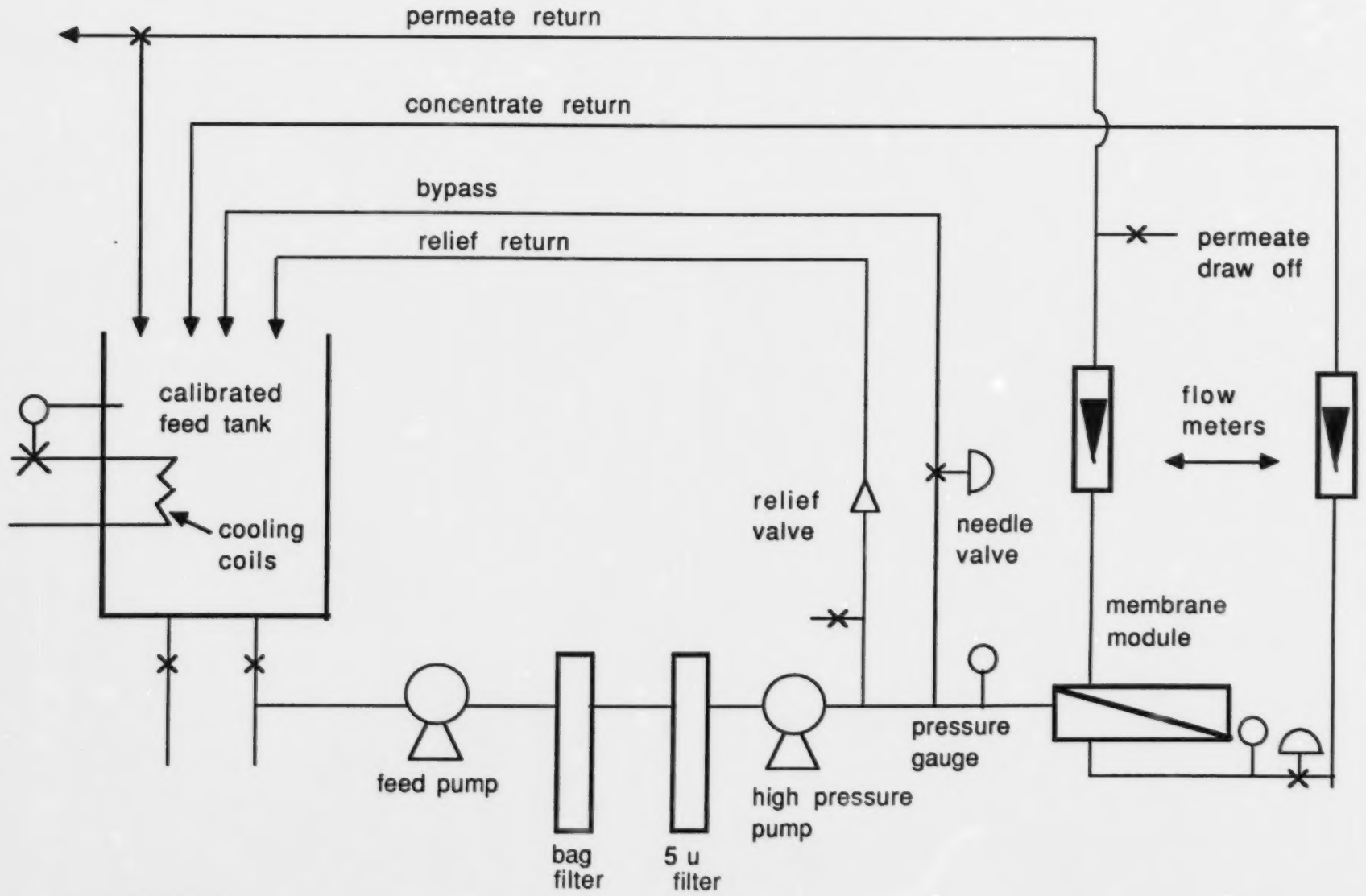
Personal protection took the form of an ABBA breathing apparatus for routine operations and a Scott air pack for emergency use. In addition, operators wore corrosion resistant overalls, boots and gloves. Regular checks by non-operating staff were conducted during testing to ensure operator protection. Non-essential personnel were allowed only limited access to the general area.

3.2 Test Procedures

3.2.1 Membrane Qualification Test

The membrane qualification test is a quality control test which is carried out at appropriate times throughout the life of a membrane. A new membrane is subjected to this test to check whether the manufacturer's performance specifications are met and determine

FIGURE 3 - 2. TEST SYSTEM FOR CONCENTRATION RUNS



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whether the membrane is acceptable. During the experimental test program, additional membrane qualification testing is carried out to assess whether the membrane is in the original condition or whether it has been damaged to any degree during use. The membrane qualification test is particularly important when treating wastewaters having unknown, possibly deleterious, effects on membranes.

The membrane qualification test is conducted with the actual test equipment and membranes used for the process test.

The procedure for the conduct of the test in this case comprised the following steps. The feed tank was filled with water which had been treated by reverse osmosis followed by deionization. Enough NaCl was added to prepare a 2500 mg/L solution. The test system was started and pressure set at 3450 kPa (500 psig) which was the desired processing pressure. The permeate flowrates were monitored at 15 minute intervals and permeate conductivity was monitored at 30 minute intervals. The test proceeded for approximately 2 hours at which time the permeate flow and conductivity stabilized. The observed membrane performance with respect to permeate flowrate and conductivity rejection at this steady state condition formed the basis for comparison with manufacturer's specifications.

3.2.2 Stability Tests

The selection of membranes for further testing was based on observed membrane performance during a stability test which was conducted with the equipment shown in Figure 3-1.

Three membranes were tested in parallel on one feed stock. The test was run at 3450 kPa (500 psig) and the feed temperature was contolled between 21-24°C. The concentrate flowrates were set at 18 L/minute for the Filmtec and Toray membranes and 24 L/min. for the Desal membrane as suggested by the respective manufacturers. Both the permeates and concentrates were returned to the feed tank.

The permeate flowrates were monitored at 15 minute intervals and the permeate conductivity at 30 minute intervals. The tests proceeded until the permeate flows and conductivities stabilized after a period of approximately one hour. Once steady state was established, a set of 1 L samples was collected for analysis. Methods of analysis are presented in Appendices A and B.

Prior to sampling, the sample lines and the sample containers were flushed with the sample to eliminate contamination.

3.2.3 Concentration Tests

The two feed stocks were concentrated with the equipment shown in Figure 3-2 but only the Toray membrane was used. The system pressure was set at 3450 kPa (500 psig) and the concentrate flowrate at 18 L/min. The temperature of the feed was controlled between 21 - 24°C. The permeate was not returned to the feed tank.

The permeate flowrate and feed volume were monitored at 15 minute intervals and samples were collected for analysis when the feed reached concentration factors of 1:1, 2.5:1, 5:1, and 10:1.

Both the permeate and the concentrate were saved for return to EMR.

3.2.4 Cleaning

After the membrane qualification tests, the test system was rinsed with RO/DI water.

After the stability test the system was rinsed with 10 L aliquots of tap water. The rinse waters containing residual cyanide were drained into a pail containing 1 to 2 L of alkaline hypochlorite. The oxidation reaction involving the cyanide and the hypochlorite produced a blue colour within seconds of contact. System rinsing was repeated until no colour change was observed. The test system was rinsed finally with tap water followed by RO/DI water. No chemical cleaning was performed since the formation of scale on the membranes was improbable considering the short duration of the test and the relatively small volume of wastewater treated.

The system clean-up procedure implemented following the concentration runs was similar to that following the stability runs. The exception was that following the run with the high pH feedstock, the system was rinsed for 30 minutes with a citric acid solution once the cyanide was eliminated from the system. The system was then rinsed with tap water followed by RO/DI water.

When not in use, the test system was filled with RO/DI water in order to keep the membranes moist overnight and over the weekends.

4.0 RESULTS AND DISCUSSION

4.1 Feedstock Quality Characteristics

Two feedstock samples, each having different characteristics, were received for testing. One feedstock sample was a gold mill barren bleed and the second was a sample of barren bleed that had been acidified and stripped of HCN by means of the acidification/volatilization (AV) process.

The summary of analytical results characterizing the quality aspects of each feedstock is presented in Table 4-1. The complete results are presented in Appendix C.

The analytical results show that both feedstocks are typical as compared to characterizations found in the literature[4]. Both feedstocks were clear with a slight yellow colour.

The alkalinity measurement, presented in Table 4-1, includes a contribution[7] by CN^-. The adjusted value of alkalinity in the barren bleed was calculated to be 810 mg/L. No adjustment of the alkalinity value reported for the other feedstock was necessary since the wastewater from the AV process contained no alkalinity due to its low pH of 2.

The concentration of $SO_4^=$ in the wastewater from the AV process was five times that observed in the barren bleed. The source of this sulphate was the sulphuric acid used to lower the pH.

The scaling potential of these feedstocks was ascertained based on a consideration of solubility products at various concentration factors, using ZENON's computer program and based on consideration of chemical equilibria. Detailed calculations are presented in Appendix E.

TABLE 4-1

Summary of the Contents of the Barren Bleed Solution and the AV Process Solution (as recieved).

Parameter (mg/l)	Barren Bleed	AV process solution
pH	10.9	2.0
conductivity (mmhos)	3.37	5.32
TDS	2700	3000
TOC	450	270
CN	660	450
CNS	320	320
Cl	160	139
SO4	400	1950
alkalinity	2060	< 1
Ca	101	93
Mg	0.3	0.35
Na	590	470
K	50	13
Cu	46	5.4
Fe	18	0.58
Ni	33	19
Zn	50	39

The pH of the barren bleed is 10.9 in the range of 10 - 11 where the $CaCO_3$ scaling is most severe. For the unconcentrated solution the scaling index was +1.43 which reflects strong scaling tendency. As the solution is concentrated, the $CaCO_3$ scaling potential increases (see Appendix E) and the $CaSO_4$ scaling potential also becomes a concern. The possible remedial measures are pH adjustment and the use of scale inhibitor. Lowering or raising the pH are two alternatives for lowering the $CaCO_3$ scaling potential. The pH would need to be raised above 12.5. However, this pH is beyond the operational limits of all RO membranes. Alternately, the pH would be required to be lowered to below 8.5. While this pH is within the operational limit of most RO membranes, the CN^- rejection, which is highly pH dependent, will deteriorate. Therefore, the use of scale inhibitor seems preferable to pH control.

The pH of the AV process solution is 2. At pH 2, $CaCO_3$ is not a problem since alkalinity is not present. Due to the relatively high concentration of Ca and SO_4, scaling by $CaSO_4$, however, is possible upon concentration. At pH 2 about 55% of the total sulfate is in the SO_4^{-2} form (see Appendix E) and the balance is in the HSO_4^- form. $CaSO_4$ is less soluble than $Ca(HSO_4)_2$ and thus more likely to scale. The bisulphate form is favored as the pH is lowered. Lowering of pH can be one method to control scaling, however, excessive amounts of acid would be required. Alternately, the use of scale inhibitors would be more economical.

Scaling can also be controlled by the seeded reverse osmosis process. This process usually applied to industrial waste waters containing extremely high levels of scaling species and is a severe

strain on equipment as about a 1% slurry would need to be circulated in the system. The circulation of slurry dictates the use of membrane in the tubular configuration. The seeded RO systems are far more expensive than equivalent systems with membranes in the spiral configuration and scale inhibitor added to the feed.

The seeded RO is not recommended as the level of scaling species is not high enough to warrant seeding and scaling could be controlled by inhibitors.

The possible effect of the observed concentration of iron was given consideration because the presence of iron may adversely affect membrane life. However, it was concluded that the potential effect of iron may be minimized because of the expected complexation with CN^- species.

4.2 Membrane Selection and Concentration Tests

Details of the test procedures were presented in Section 3.2. The order in which the tests were conducted is as follows:

- Membrane qualification test No. 1
- Membrane selection test at high pH
- Membrane qualification test No. 2.
- Membrane qualification test No. 3.
- Replaced the Desal-1 membrane with Desal-2
- Membrane selection test at low pH
- Membrane qualification test No. 4
- Concentration test at high pH
- Membrane qualification test No. 5
- Concentration test at low pH

° Membrane qualification test No. 6

The summary of results from the membrane qualification tests is presented in Appendix D.

4.2.1 Membrane Selection

The summary of results of the membrane selection tests are found in Tables 4-2 and 4-3 and additional related information is presented in Appendix C.

An inspection of Table 4-2 reveals that, with the barren bleed feedstock, the best rejection of all species was obtained with the Toray membrane. Approximately 93% rejection of CN^- and approximately 96% rejection of CNS were achieved. Interestingly, the rejection of TOC was observed to correlate very closely with the rejection of CN^- even though organics were not present. Thus, it was concluded that TOC could be used to estimate both CN^- rejection and concentration if no organics are present in the wastewater.

After single stage treatment, the concentration of CN^- in the permeate from the Toray membrane was observed to be 50 mg/L which is still too high for discharge. However, it must be remembered that a reduction in the CN^- and CNS concentrations by at least an order of magnitude is attainable through dual stage treatment. The resulting effluent would possibly meet the 1 mg/L target effluent concentration for CN^- (McNamara[5]).

With the exception of zinc, the concentrations of heavy metals in the permeate from the Toray membrane were below the

TABLE 4-2

Summary of membrane selection test data with the Barren Bleed Solution

Parameter (mg/l) *	Feed level	FT-30 permeate level	FT-30 permeate % Rejection	Desal-1 permeate level	Desal-1 permeate % Rejection	Toray permeate level	Toray permeate % Rejection
Flux (m3/m2-d)		1.0		1.8		0.65	
Flux (usgfd)		25		45		16	
pH	10.37	10.25		10.8		10.83	
conductivity (mmhos)	2.52	0.97	61.5	0.764	80.9	0.329	86.9
CN	760	240	68.4	150	80.2	50	93.4
CNS	130	49	62.3	37	71.5	4.8	96.3
TOC	403	105	73.9	79	80.4	28	93
Cl	160	48	70	25	84.4	0.17	99.9
SO4	430	130	69.8	63	85.3	0.14	99.97
Ca	66	21	68.2	10	84.8	0.09	99.9
Mg	0.37	0.13	64.8	0.05	86.5	<.05	> 86.5
Na	600	220	63.3	160	73.3	57	90.5
K	45	16	64.4	10	77.8	4.7	89.5
Cu	48	15	68.7	7.1	85.2	< .006	100
Fe	18	5.9	67.2	2.7	85	< .01	> 99.9
Ni	34	11	67.6	5	85.3	< .009	100
Zn	51	16	68.6	7.6	85.1	0.02	99.9

* or otherwise noted

TABLE 4-3

Summary of membrane selection test data with the AV Process Solution

Parameter (mg/l) *	Feed level	FT-30 permeate level	FT-30 permeate % Rejection	Desal-1 permeate level	Desal-1 permeate % Rejection	Toray permeate level	Toray permeate % Rejection
Flux (m3/m2-d)		1		1		1	
Flux (usgfd)		25		25		25	
pH	2.16	2.7		3.68		5.69	
conductivity (mmhos)	4.4	1.51	65.7	0.478	89.1	0.048	98.9
CN	340	265	22.1	250	26.5	220	35.3
CNS	130	54	58.5	15	88.5	7.5	94.2
TOC	240	186	22.5	175	27.1	150	37.5
Cl	110	32	70.9	9	91.8	1	99.1
SO4	1400	460	67.1	130	90.7	0.95	99.9
Ca	100	29	71.0	8.6	91.4	0.12	99.9
Mg	2.6	0.73	71.9	0.21	91.9	< .05	> 98.1
Na	520	170	67.3	63	87.9	8.6	98.3
K	36	11	69.4	4.3	88.1	< .4	> 98.9
Cu	5.7	1.7	70.2	0.58	89.8	0.26	95.4
Fe	1.1	0.88	20.0	0.09	91.8	< .01	> 99.1
Ni	19	5.5	71.1	1.7	91.1	< .009	> 99.9
Zn	38	9.9	73.9	3.1	91.8	0.007	100.0

* or otherwise noted

detection limit. Accordingly, the discharge limit of 0.3 - 0.4 mg/L (McNamara[5]) for heavy metals was considered to have been met.

For tests done with low pH water from the AV process, the Desal-1 membrane was replaced with the Desal-2.

The results of the membrane selection tests done with the water from the AV process is presented in Table 4-3. The best rejections were obtained with the Toray membrane, as was the case during the run with the barren bleed. This time however, 35% CN^- rejection and 94% CNS rejection was achieved. At low pH the CN^- exists in the associated form and thus its degree of rejection was reduced. Again, the reverse osmosis system could be staged to further reduce the level of CN and CNS. If the water quality is not satisfactory for discharge, then the water could be recycled for use (McNamara, 1986). The level of heavy metals in the permeate was about 0.6 mg/L. This level is slightly above the 0.4 mg/L limit for discharge and further treatment to reduce CN^- and CNS levels will also reduce the levels of heavy metals.

The flux data are shown in Tables 4-2 and 4-3. The flux is the measure of permeate flow rate per unit area of membrane surface. The most commonly used unit of flux is U.S.gfd, U.S. gallons per square foot - day. The metric equivalent is cubic meters per square meter - day. The Toray membrane permeated at the lowest rate of 0.65 m^3/m^2-d (16 U.S.gfd) during the run with the barren bleed and at the same rate as the other membranes during the run with the water from the AV process. Even though the Toray membrane showed somewhat lower permeation rates than the other membranes its superior rejection make it the choice for further testing.

The salt flux data from membrane qualification test runs No.'s 1, 2, 3, and 4 show that there was no decline in flux or salt rejection. The indications are that there was no membrane deterioration during these short runs.

4.2.2 Solution Concentration

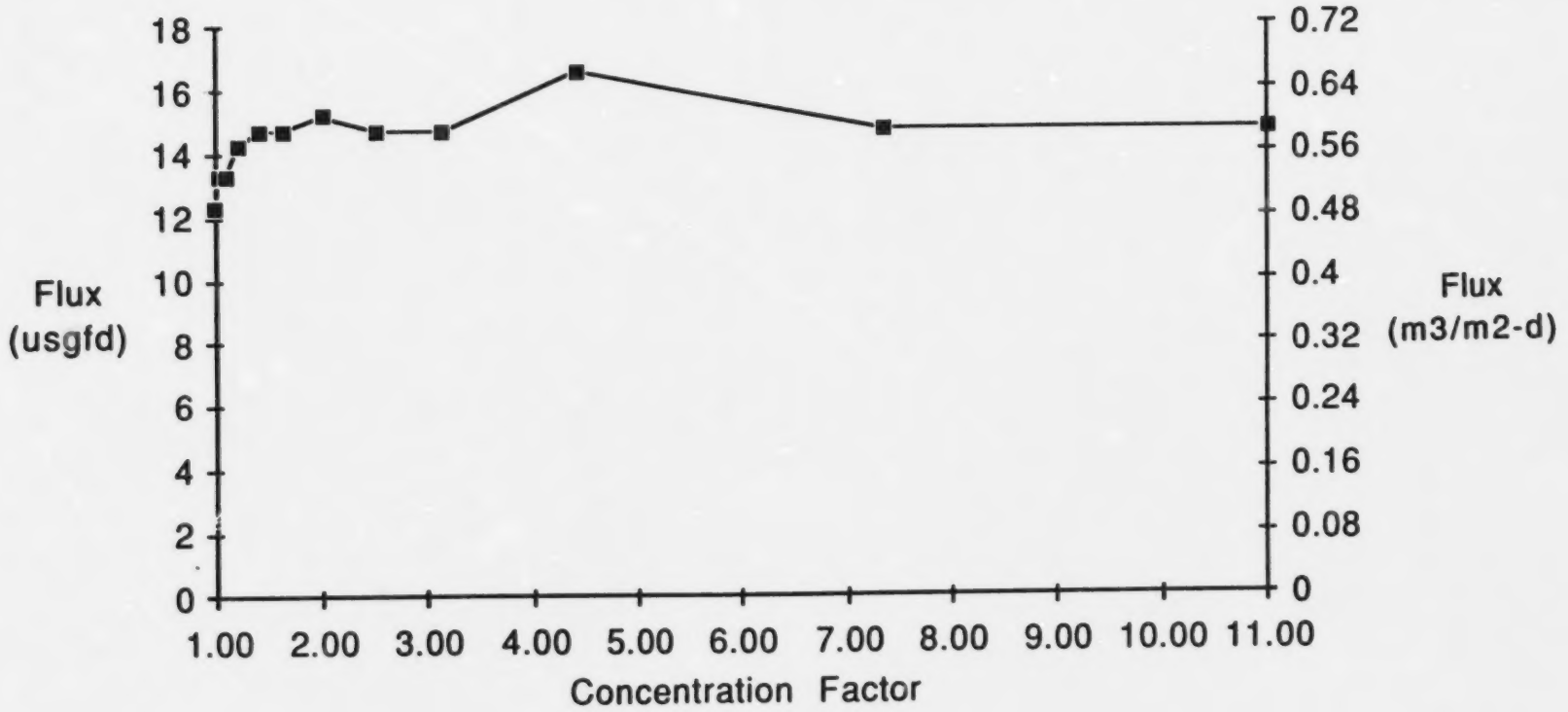
For the concentration runs, the Filmtec and Desal membranes were taken out of the test system and the Toray membrane was undisturbed.

The feed tank was filled and the permeate line placed into the now empty 200 L (45 gal.) drum and the reject was returned to the feed tank. The concentration began and the contents of the second 200 L (45 gal.) drum was added to the feed tank by 20 - 30 L increments. When the volume reduction reached the equivalent concentration factors of 2.5, 5, and 10 to 1, samples were taken for analysis. The data representing the unconcentrated sample was taken from the membrane selection tests.

The permeate flux for the barren bleed using the Toray membrane was plotted as a function of concentration factor and is presented in Figure 4-1.

During the run with the barren bleed, the flux rose from an initial 0.43 m^3/m^2-d (12 U.S.gfd) to about 0.6 m^3/m^2-d (15 U.S.gfd) as the temperature in the feed tank stabilized at about 20°C. The flux remained at 0.6 m^3/m^2-d (15 U.S.gfd) for the balance of the run even though an eleven fold volume reduction was achieved. The steady flux indicates that fouling or scaling did not occur, however, the short duration of the test and the small volume of water (440 L) may have

Figure 4-1
Performance of the Toray membrane during the
Barren Bleed Concentration Run



precluded the occurrence of scaling. Computer predictions (Section 4.1) indicated scaling can be expected.

Figure 4-2 presents a plot of the permeate flux and temperature as a function of concentration factor, for tests using the AV process effluent and the Toray membrane.

As shown in the Figure, the initial permeate flux was 0.99 m^3/m^2-d (24.5 U.S.gfd). The flux increased slowly as the temperature stabilized at about 20°C. At that point the cooling water flow was lost. By the time the cooling water was restored, the temperature in the feed tank rose 10°C. By the end of the run the temperature was down to 24°C. The permeate flux was sensitive to temperature as the rising temperature reduced the viscosity of the water and thus allowed the water to flow through the membrane pores at a faster rate. Nevertheless, the trend in the data shows a declining flux with increasing concentration. The decline in flux could be caused by scaling or an increase in osmotic pressure due to concentration. The final flux is expected to be about 0.73 m^3/m^2-d (18 U.S.gfd) when corrected to 20°C.

The analytical results of samples taken during the concentration runs are presented in Tables 4-4 and 4-5. For barren bleed samples, (Table 4-4) the CN rejection decreased from 93.4% to 90.0% and CNS rejection increased from 96.3% to 98.9% over the 10 fold concentration. The rejection of anions and metals remained virtually the same.

It is obvious from Table 4-4 (and also Table 4-5) that 10 fold volume reduction did not result in a 10 fold increase in concentration. During reverse osmosis concentration tests, it is

Figure 4-2
Performance of the Toray Membrane during
the AV Process Effluent Concentration Run

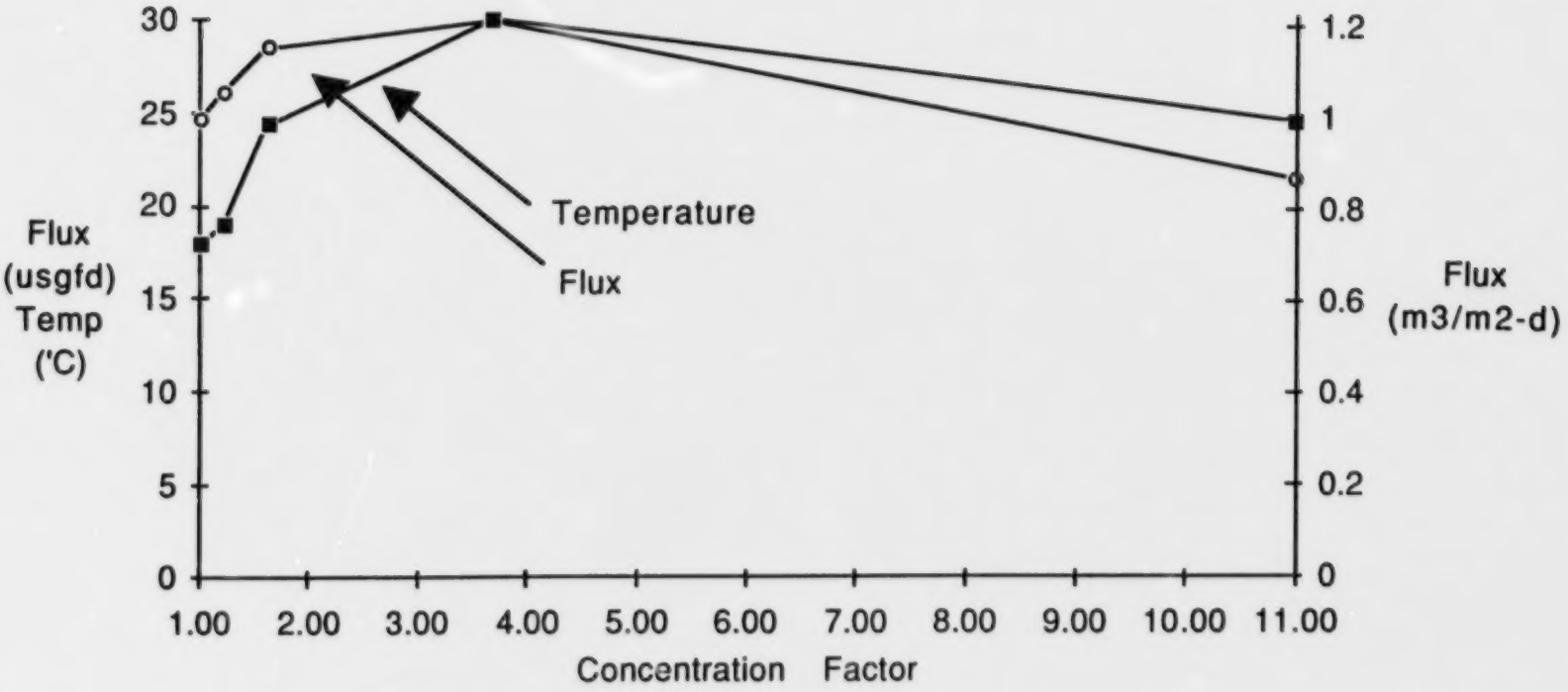


TABLE 4-4

Summary of Concentration Test Data on Barren Bleed with the Toray membrane

CF*	Parameter (mg/l)	Feed/ Concentrate	Permeate	% Rejection
1**	pH	10.3	10.83	
	conductivity (mmhos)	2.52	0.329	86.9
	CN	760	50	93.4
	CNS	130	4.8	96.3
	TOC	403	28	93.1
	Cl	160	0.17	99.9
	SO4	430	0.14	100.0
	Ca	66	0.09	99.9
	Na	600	57	90.5
	Cu	48	< .006	100.0
	Fe	18	< .01	>99.9
	Ni	34	< .009	100.0
	Zn	51	0.02	100.0
2.5	pH	10.09	10.53	
	conductivity (mmhos)	6.11	0.51	91.7
	CN	1730	96	94.5
	CNS	450	5.4	98.8
	TOC	890	56	93.7
5	pH	10.0	10.45	
	conductivity (mmhos)	9.67	0.907	90.6
	CN	2460	200	91.9
	CNS	600	7.1	98.8
	TOC	1170	97	91.7
10	pH	9.82	10.42	
	conductivity (mmhos)	14.22	1.578	88.9
	CN	3700	370	90.0
	CNS	1100	12	98.9
	TOC	1810	230	87.3
	Cl	1100	6.5	99.4
	SO4	3000	1.5	100.0
	Ca	230	4.1	98.2
	Na	5020	330	93.4
	Cu	340	0.18	99.9
	Fe	120	0.07	99.9
	Ni	220	0.14	99.9
	Zn	260	0.22	99.9

* CF : Concentration Factor

** 1= no. concentration

TABLE 4-5

Summary of Concentration Test Data on Solution from Acidifier/Stripper with the Toray membrane

CF*	Parameter (mg/l)	Feed/ Concentrate	Permeate	% Rejection
1**	pH	2.16	5.69	
	conductivity (mmhos)	4.4	0.48	89.1
	CN	340	220	35.3
	CNS	130	7.5	94.2
	TOC	240	150	37.5
	Cl	110	1	99.1
	SO4	1400	0.95	99.9
	Ca	100	0.12	99.9
	Na	520	8.6	98.3
	Cu	5.7	0.26	95.4
	Fe	1.1	< .01	>99.9
	Ni	19	< .009	100.0
	Zn	38	0.007	100.0
2.5	pH	2.19	4.11	
	conductivity (mmhos)	9.8	0.135	98.6
	CN	290	250	-
	CNS	420	24	94.3
	TOC	310	210	32.3
5	pH	1.96	4.04	
	conductivity (mmhos)	16.22	0.278	98.3
	CN	600	250	58.3
	CNS	790	54	93.2
	TOC	420	200	52.4
	Cl	480	17	96.5
	SO4	6200	6	99.9
	Ca	390	6.1	98.4
	Na	1490	43	97.1
	Cu	17	0.16	99.1
	Fe	3.1	0.01	99.7
	Ni	67	0.03	100.0
	Zn	130	0.09	99.9

* CF : Concentration Factor
** 1 = no. concentration

TABLE 4-5
(continued)

Summary of Concentration Test Data on Solution from Acidifier/Stripper with the Toray membrane

CF*	Parameter (mg/l)	Feed/ Concentrate	Permeate	% Rejection
10	pH	1.89	3.49	
	conductivity (mmhos)	23.94	0.459	98.1
	CN	970	290	70.1
	CNS	950	150	84.2
	TOC	730	230	68.5
	Cl	960	32	96.7
	SO4	12000	11	99.9
	Ca	360	0.49	99.9
	Na	5200	93	98.2
	Cu	25	0.11	99.6
	Fe	4.5	< .01	>99.9
	Ni	130	0.08	99.9
	Zn	220	0.14	99.9

* CF : Concentration Factor

typically not possible to obtain an accurate material balance based on grab sampling. There is solute movement across the membrane in the permeate and there could be precipitates formed that could elude analysis. On large scale reverse osmosis systems, the membrane modules can be staged to retain virtually all of the solutes of interest.

In the water from the AV process the CN rejections increased from 35.3% to 70.1% and CNS rejections decreased from 94.2% to 84.2% over a 10 fold reduction in volume. Rejections of anions and metals remained virtually the same over the same concentration range.

In the AV process effluent, the cyanides exist complexed with metals. While the metals are nearly completely rejected the rejection of cyanide was substantially lower. It was expected that the rejection of metals and cyanides would be identical. This discrepancy could arise from the destruction of metal cyanide complexes by mechnical means in the RO system. Turbulence in the pump or in the system and extensive recirculation in bench scale testing could combine to cause degradation to a higher degree than would be experienced in a once through system. Apparantly, mechanical means are used in conventional methods of destruction of metal cyanide complexes (McNamara[5]).

Salt flux tests no's 4, 5, and 6 show that salt rejection and permeate flux did not deteriorate over the duration of the tests. Therefore, in these short test no appreciable scale was formed on the membrane.

5.0 DESIGN AND ECONOMICS

The results of the reverse osmosis tests outlined in Section 4.2 were used to form the basis to design a pilot plant and to design a 1,000 tonne/day reverse osmosis system for process economics evaluation.

The reverse osmosis system must concentrate the feed 10 fold and produce a dischargeable or recycleable final effluent.

The RO system may be used in three different modes. As one possible mode, a single RO system could preceed the AV process. Alternately, in addition to the unit preceeding the AV, a second RO could be added following the AV. Finally, a third option could incorporate one RO system after the AV, without prior concentration. The tests done here (Section 4.2) produced data to allow fairly good estimations for modes 1 and 3, and to allow some prediction for mode 2. Pilot plant work will be required prior to final design of any full scale system.

5.1 Pilot Plant

5.1.1 Pilot Plant Concept

During the short test described in this report (Section 4.2) membrane scaling or fouling was not observed even though predicted by ZENON's computer simulation of feed concentration. With small volumes of samples the long term effects on the membrane cannot be determined. Several months of continuous operation is required to properly assess membrane performance. The long term tests are best carried out with pilot scale equipment on site.

The pilot scale reverse osmosis system proposed must be flexible enough to allow the assessment of long term membrane performance in the three modes of operation previously described. At the same time the pilot scale RO system must achieve 10 fold feed concentration and produce an environmentally acceptable effluent or recycleable water.

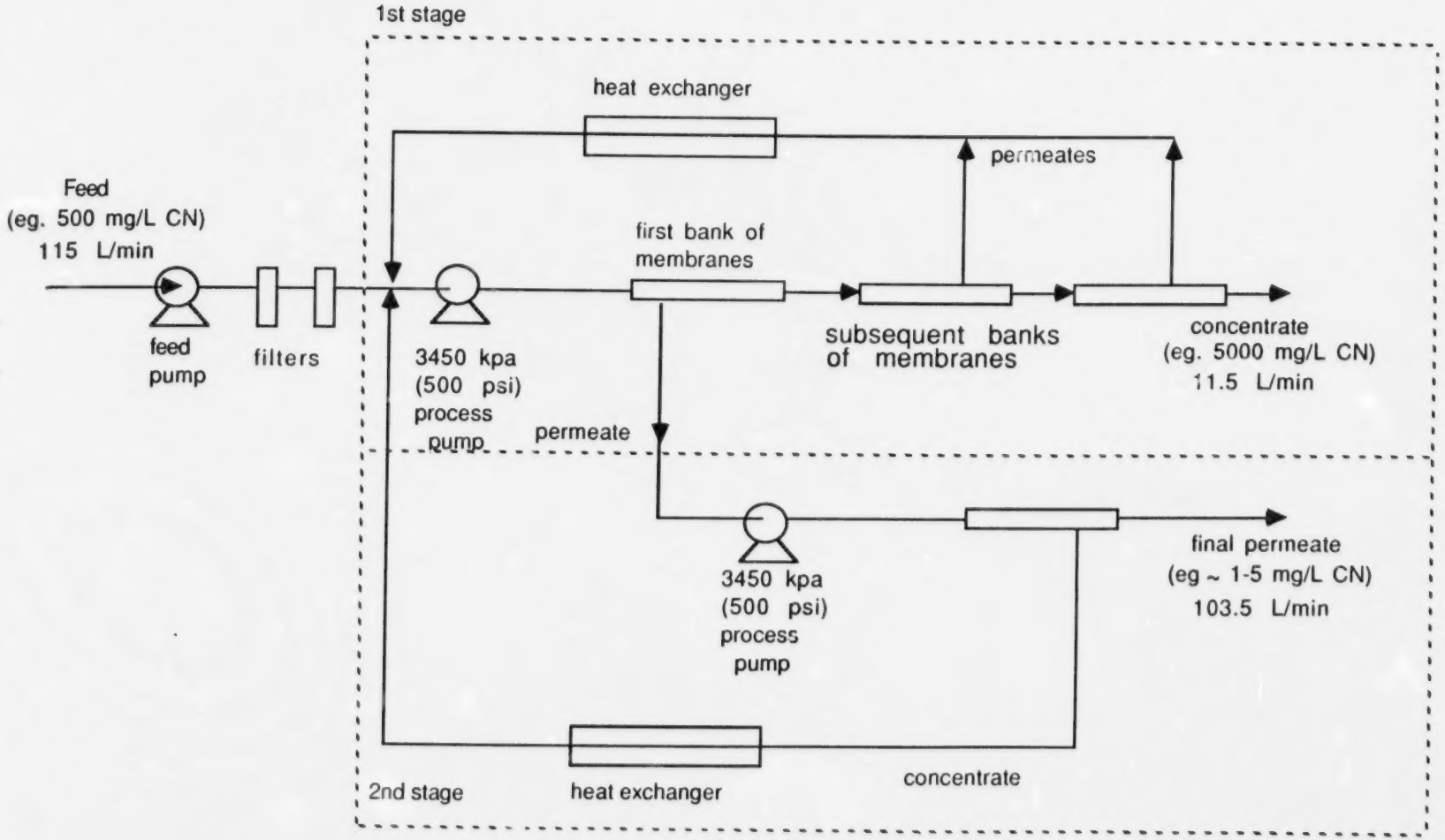
The concept of the pilot scale RO system is presented in Figure 5-1. The developed process was based on the results presented in Section 4.2 and system performance requirements.

With 90% CN rejection in a single pass, a CN level of 50 mg/L was obtained from an unconcentrated feed. At 10 fold concentration the CN level in the permeate resembled that of the original feed. Therefore, a double stage RO system is proposed.

As shown in Figure 5-1, the first stage consists of several banks of membranes in a tapered layout. The barren bleed is concentrated in the first stage system in a single pass. The reject stream of the last bank of membrane is fed to the AV process. The concentrate would pass through the system only once and therefore the destruction of metal cyanide complexes will be minimized. The permeate from all but the first bank of membranes is returned to the system intake. The permeate from the first bank of membranes, which should contain about 50 mg/L CN, is fed to the second stage system where the level of CN is expected to be further reduced by an order of magnitude. The permeate from the second stage may be directly dischargeable or reusable. The reject stream from the second stage is fed back to the first stage intake.

FIGURE 5-1

SCHEMATIC OF THE PILOT PLANT CONCEPT



In this manner, both feed concentration and effluent polishing is achieved.

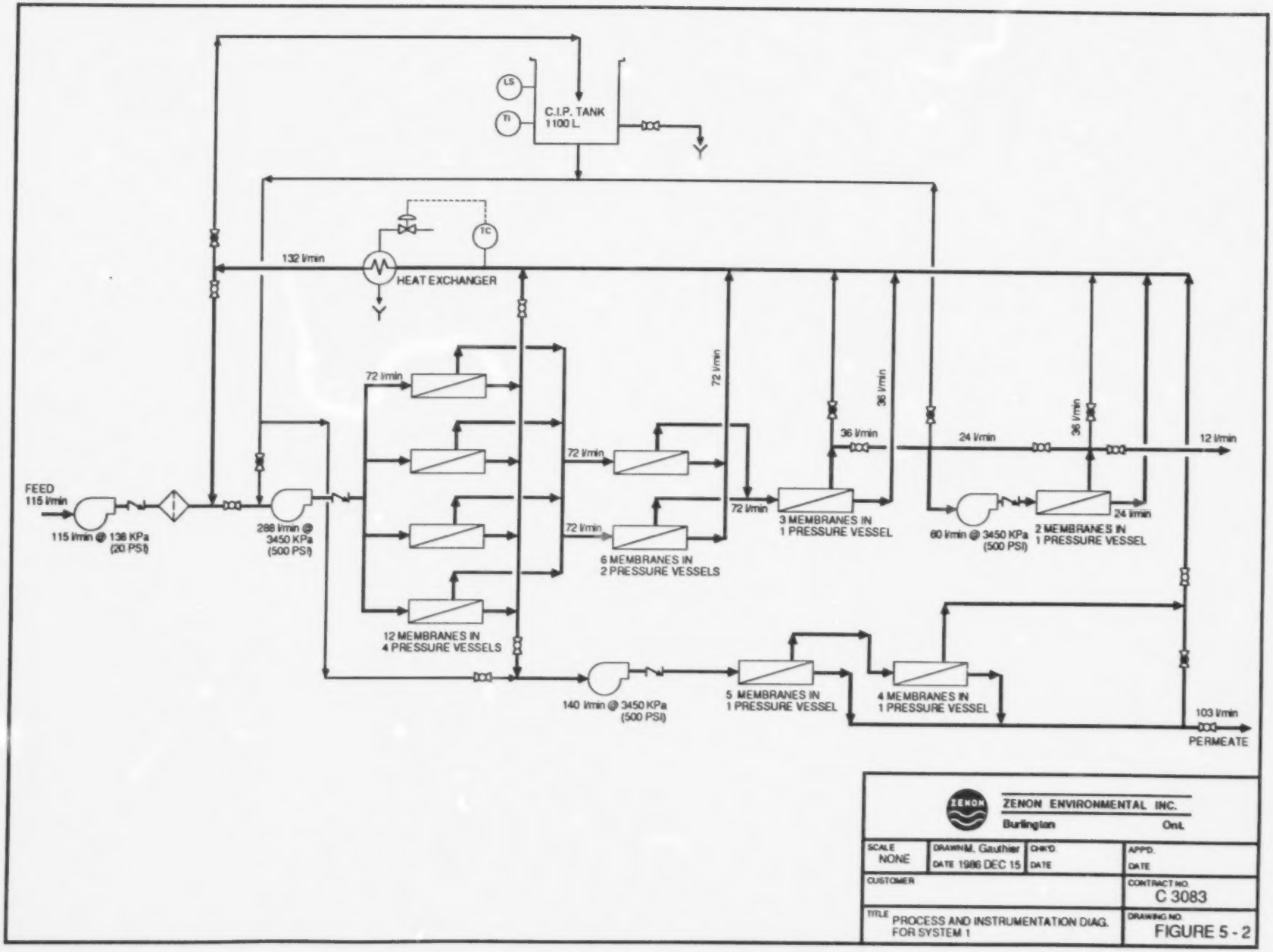
The pilot plant will include the necessary heat exchangers, prefilters to protect the pump and membranes in case of solids in the feed, process and supply pumps and clean in place (CIP) system. A surge feed tank may be required when the pilot plant will operate in modes 2 and 3, in the event that the AV process cannot supply the required volume of feed to the RO system.

5.1.2 Proposed Pilot Plant

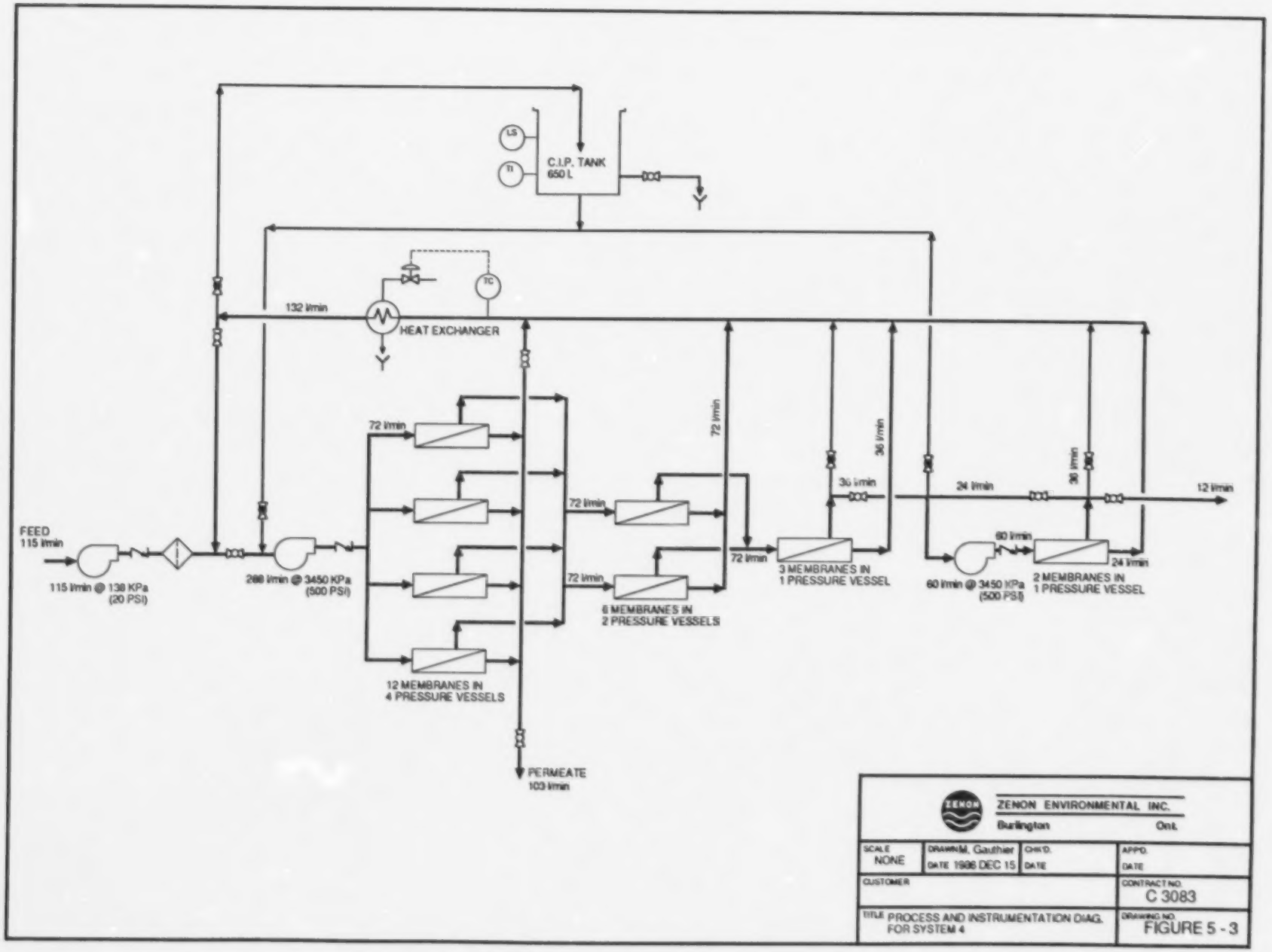
The pilot plant concept presented in Figure 5-1 was converted to the design of an actual pilot plant shown in Figure 5-2. Three versions of this pilot plant that completely satisfy the requirements listed in Section 5.1.1 were considered. The diagram shows System 1 with a 115 L/min (25 igpm) feed flowrate. System 2 with a flowrate of 40 L/min (10 igpm) and System 3 with 20 L/min (5 igpm) feed flowrate were also designed and costed. The systems are identical in layout and only the size of pumps and piping and the number of membranes used are different.

The systems include the necessary pumps, membrane modules, pressure vessels, instrumentation, electricals, heat exchanger, clean-in-place (CIP) system and support structure.

An additional system was designed and shown in Figure 5-3. System 4 is similar to System 1 with the difference that the second stage RO was eliminated. If the permeate from the first stage RO is of sufficient quality (approx. 500 mg/L CN, metals at trace levels) for in plant reuse then System 4 would satisfy the process objectives.



ZENON ENVIRONMENTAL INC. Burlington Ont.			
SCALE NONE	DRAWN M. Gauthier DATE 1986 DEC 15	CHK'D DATE	APP'D DATE
CUSTOMER			CONTRACT NO. C 3083
TITLE PROCESS AND INSTRUMENTATION DIAG. FOR SYSTEM 1			DRAWING NO. FIGURE 5 - 2



ZENON ENVIRONMENTAL INC. Burlington Ont.			
SCALE NONE	DRAWN M. Gauthier DATE 1998 DEC 15	CHK'D. DATE	APP'D. DATE
CUSTOMER			CONTRACT NO. C 3083
TITLE PROCESS AND INSTRUMENTATION DIAG. FOR SYSTEM 4			DRAWING NO. FIGURE 5 - 3

The costs of the four systems are presented in Table 5-1.

The estimated cost includes all subcomponents, assembly labour, engineering, quality control and testing. The operation and maintenance costs include cost of electrical energy at $0.05/kw-hr, labour and materials for routine maintenance at 6% of capital cost (excluding the membranes), membrane replacement at every 3 years on average, necessary chemicals for cleaning, process cooling cost assumed to be 5% of motor electrical energy, and other labour at $26/hr. The operating year is set at 325 days.

The cost of System 1 is estimated at $214,200. Three other versions of the pilot plant were developed for cost comparison purposes. The evaluation of System 4's suitability will require in addition to economic consideration the assessment of water quality requirements. The costs for down sized systems can be developed at a later date if required.

The major portion of the operation and maintenance is the cost of membrane replacement and process energy. The three year membrane life is a rule of thumb figure and could only be refined during pilot scale tests. The annual operation and maintenance (O & M) costing is not completely applicable to pilot scale systems as their mode of operation will depend on the scope and length of the test program. Normally, pilot plant testing requires close operator attention and therefore the normal O & M procedures would be covered under the test program as one of the determinations.

Table 5-1 Costs of the Pilot Plant Options

System	1	2	3	4
Feed rate (L/min)	115	40	20	115
Capital cost ($)	214,230	117,810	89,010	116,740
Membrane replacement ($/yr)	20,480	7,680	3,860	14,720
Process energy costs ($/yr)	24,690	10,140	4,950	20,360
Process cooling costs ($/yr)	1,200	510	250	1,020
Cleaning chemicals ($/yr)	6,900	4,600	3,450	6,900
Labor-Cleaning & Operating ($/yr)	16,900	16,900	16,900	16,900
Maintenance-Labor & Parts ($/yr)	9,170	5,690	4,650	4,350
Total - O & M ($/yr)	79,340	45,520	34,060	64,250

5.2 Process Economics

The barren bleed production of a medium size gold extraction installation is typically 1000 tonne/day. The economics of the AVR process will be evaluated for a plant of this size (McNamara, 1986). Therefore, a 1000 tonne per day reverse osmosis system to concentrate the barren bleed and to produce an environmantally acceptable final effluent was designed and costed. The system layout is similar to that of the pilot System 1 shown in Figure 5-2 and was based on the identical design criteria. The system is predicted to reduce the volume of barren bleed sent to the AVR by 10 fold, and recover 99% of the cyanide in the original barren bleed while producing an environmentally acceptable final permeate. The concentration of cyanide in the final permeate is estimated to be around 5 mg/L. All but a trace amount of metals will be retained by the RO system. Since the estimates of performance of the double stage RO system were based on bench scale tests it is necessary to optimize the system operating parameters through long term pilot scale testing.

The costs of this RO system are presented in Table 5-2. The capital cost of the complete 1000 tonne/day RO system is estimated at $815,500, and includes the cost of necessary pumps, piping, valves, instrumentation, electricals, membranes, pressure vessels, support frame, engineering, and assembly labour.

The operation and maintenance costs include membrane replacement at 3 year intervals on average, process energy requirements at $0.05/kw-hr, process cooling at 5% of process energy consumption, cleaning chemicals, labour for cleaning at $26/hr and routine maintenance parts and labour at 6% of capital cost excluding

Table 5-2 Predicted Costs of the 1000 Tonne/day RO System

Feed rate (L/min)	700
Capital cost ($)	815,500
Membrane replacement ($/yr)	115,200
Process energy costs ($/yr)	65,400
Process cooling costs ($/yr)	3,270
Cleaning chemicals ($/yr)	23,000
Labor-Cleaning & Operating ($/yr)	16,900
Maintenance-Labor & Parts ($/yr)	28,190
Total - O & M ($/yr)	251,960

the membranes. It is possible to obtain a warranty service contract from ZENON at a rate of about 5%/yr of the total capital cost.

The operation and maintenance costs were developed from ZENON's extensive experience in manufacturing and servicing RO systems. On a unit such as proposed here, the actual O & M costs may vary. Both the capital and O & M costs were developed for a system designed on data obtained from bench scale tests. Therefore, the system design is not optimized and the O & M procedures are not tested. The complete system performance and the effectiveness of O & M procedures must be determined on pilot scale test system.

In comparison with the 115 L/min pilot plant, the flow capacity of the full scale plant (1000 tonne/day) increased about 6 fold but the capital cost and O & M costs increased only 4 fold and 3 fold, respectively. The cost of engineering, design, assembly and labour for cleaning remained nearly identical through the scale up. The size of pumps and piping becomes more cost effective at larger sizes. Only the number of membranes, pressure vessels and supplies increased proportionally to flow capacity.

6.0 CONCLUSIONS

The following conclusions may be drawn from this study.

i) The Toray membrane proved superior.

ii) Total cyanide rejections of 93% were obtained from the unconcentrated barren bleed and 35% from the unconcentrated acidified and stripped barren bleed. At 10:1 concentration, 90% and 70% rejections, respectively were obtained.

iii) Thiocyanate rejections of 96% were obtained from the unconcentrated barren bleed and 94% from the unconcentrated acidified and stripped barren bleed. At 10:1 concentration, 99% and 84% rejections, respectively, were obtained.

iv) Metals were nearly completely rejected from both cyanide solutions.

v) At the concentration factor of 10 the permeate quality did not significantly deteriorate from the permeate quality produced at no concentration.

vi) Concentration factors of greater than 10 could be achieved as flux decline was non-existent or was insignificant during the concentration runs. Initial flux of0.65 $m^3/^2/d$ (16 U.S.gfd) was obtained from the barren bleed and 1 $m^3/m^2/d$ (25 U.S.gfd) from the AV processed water.

vii) Both the barren bleed and acidified and stripped barren bleed are capable of being treated by RO.

viii) Both cyanide concentration and cyanide reduction for environmental concerns can be achieved with a double pass reverse osmosis system.

ix) Pilot plant design based on the data produced here was possible.

x) The prediction of the performance and cost of a 1000 tonne/day RO system must be confirmed and optimized through pilot scale testing.

7.0 RECOMMENDATIONS

The present study showed that cyanide concentration and the production of an environmentally acceptable effluent from barren bleed was feasible by the reverse osmosis process. However, the data collected to date is not sufficient to design a full scale installation. The process, equipment, and operation and maintenance procedures need to be optimized. Membrane scaling, a serious concern for all RO systems cannot be studied adequately on a bench scale, and system operation and O & M procedures depend on the degree of scaling. As a result, the long term operation and performance of a complex system such as the one proposed here cannot be determined based on bench scale tests. A complete pilot scale RO system will therefore be required to properly test membrane scaling, optimize system operation, and determine O & M requirements. It is recommended that pilot scale testing proceed.

The pilot scale tests should be carried out for at least three months in each of the three modes listed in Section 5.0. In this manner, operational problems or difficulties will surface and can be corrected or compensated for in the design of the full scale system. The determination of the type and dosage of scale inhibitor will need to be done at this time. The pilot scale test program should be flexible enough to allow the investigation of problems and improvements as they develop.

To minimize the cost of the pilot plant, the smallest possible system should be built, such as System 3 shown in Section 5.1.2. The size of the pilot plant may be dictated by gold industry standards. Any of the 3 systems presented in Section 5.1.2 will be

suitable for this purpose.

During the pilot study a water use audit should be carried out at a willing gold extraction plant to determine the best and most cost effective use of their water and to aid in the design and construction of the most suitable treatment plant.

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APPENDIX A

ANALYTICAL METHODS

A.1 Total Cyanide (CN_T)

The levels of total cyanide (CN_T) were determined by means of NAQUADAT Method No. 06601 (Environment Canada, 1979). Details of this protocol are presented in Appendix B. The detection limit obtainable for CN_T is 2 ug/L.

A.2 Thiocyanate (CNS^-)

Thiocyanate concentration were determined by method 412 L (Standard Methods 1985). The determination utilizes the intense red colour produced by the complexation of CNS^- by Fe^{+3}. The detection limit of this method is 0.1 mg CNS^-/L.

A.3 Cation Scan

The levels of metals were determined by Inductively Coupled Argon Plasma (ICAP) spectroscopy. The detection limits for the cations under consideration are listed in Table A-1.

A.4 Anion Scan

The level of anions were determined by Ion Chromatography (IC). The detectable anions and the respective detection limits are listed in Table A-2.

A.5 Total Organic Carbon (TOC)

The TOC in the samples were determined with a Beckman Model 915B Total Carbon Analyzer. The detection limit of the instrument is 2 mg/L.

A.6 Alkalinity

Total alkalinity determinations were made by means of Standard Method 403 (Standard Methods, 1985). Attention is draws to the fact that the measured value may include contributions from bases such CN^-.

A.7 pH

The pH was measured with an Extech Model 541 (Extech Inc., Boston, Mass.) digital pH meter.

A.8 Turbidity

Turbidity determinations were made with the model DRT 1000 (HF Instruments, Division of Shaban Manufacturing, Fort Meyers, FL.) turbidity meter.

A.9 Conductivity

Conductivity determinations were made with a YSI Model 32 (Yellow Springs Instruments Co. Inc., Yellow Springs, Ohio) conductance meter.

TABLE A-1

Anions Detected by ICAP and Their Respective Detection Limits

Metal	Detection Limit (mg/L)
Al	0.03
Ba	0.002
Bc	0.0003
B	0.01
Cd	0.002
Ca	0.05
Cr	0.004
Co	0.01
Cu	0.006
Fe	0.01
Pb	0.04
Mg	0.05
Mn	0.005
Mo	0.02
Ni	0.009
P	0.1
K	0.1
Si	0.05
Ag	0.01
Na	0.05
Sr	0.001
Th	0.02
Ti	0.01
V	0.02
Zn	0.005
Zr	0.01

TABLE A-2

Anions Detectable by IC and Their Detection Limits

Anions	Detection Limits (mg/L)
F	0.05
Cl	0.05
NO_2 - N	0.1
Br	0.04
NO_3 - N	0.1
PO_4	0.04
SO_4	0.05

APPENDIX B

ANALYTICAL METHOD FOR CYANIDE DETERMINATION

CYANIDE
(Colorimetric–Chloramine-T, Pyridine-Pyrazolone)

1. Scope and Application

1.1. This method is applicable to the determination of cyanide in surface, waste and sea water. When the distillation assembly described is used the method is sensitive to about 2 µg/L.

2. Principle and Theory

2.1. Distillation of the sample in the presence of sulphuric acid converts complex cyanides into hydrocyanic acid, HCN. The HCN gas is absorbed in a solution of sodium hydroxide and the cyanide is determined colorimetrically.

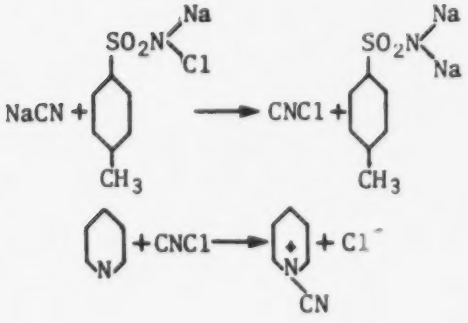
Equations:

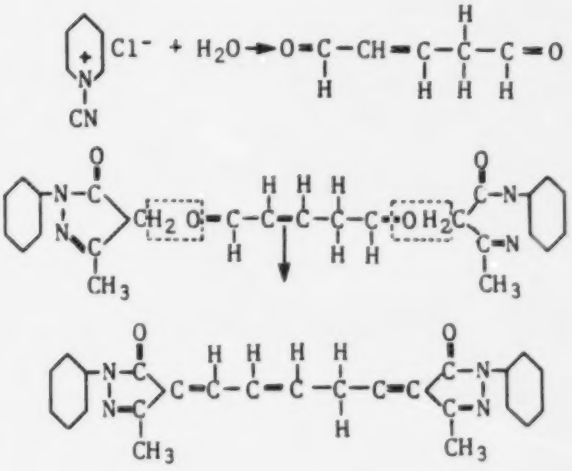
$$Fe(CN)_6^{4-} + 6H^+ \longrightarrow 6HCN + Fe^{2+}$$

$$HCN + NaOH \longrightarrow NaCN + H_2O$$

2.2. In the colorimetric measurement, the cyanide in the sodium hydroxide solution after distillation is converted to cyanogen chloride, CNCl, by reaction with chloramine-T, $CH_3C_6H_4SO_2NClNa\cdot 3H_2O$. The CNCl then forms a blue dye on the addition of pyridine-pyrazolone ($C_{10}H_{10}N_2O$) reagent and the absorbance is measured at 620 nm.

The reaction may be expressed by the following equations (ref. 11.4):





3. Interferences

3.1. Sulphides interfere and should be removed prior to distillation (see section 5).

3.2. Other interfering substances are removed by distillation.

4. Sampling Procedure and Storage

4.1. The sample should be collected in a 2-L plastic bottle and analyzed as soon as possible after collection.

4.2. Samples should be preserved by addition of sufficient NaOH to raise the pH to 11.0 or above, and be stored in a cool place.

5. Sample Preparation

5.1. Decant a sample aliquot for distillation.

5.2. Sulphide is removed by treating the alkaline sample at pH 11.0 with small increments of powdered lead carbonate, $PbCO_3$. Black lead sulphide precipitates in samples containing sulphide. Repeat this operation until no more lead sulphide forms. Filter and rinse the precipitate, add the rinse water to the filtrate, and use an aliquot for analysis. Avoid a large excess of lead

carbonate and a long period of contact in order to minimize complexing or occlusion of the cyanide with the precipitated material.

6. Apparatus

6.1. A 1000-mL three-necked flask fitted with ground-glass joints; to the three necks are fitted a thistle funnel which extends below the liquid level, an air sparging tube drawn to a fine tip, and a Friedrichs condenser (Fig. 1).

6.2. Heating mantle.

6.3. Magnetic stirrer-plate and stirring bar.

6.4. Gas absorption column made from Pyrex tubing, 22 mm I.D. and 450 mm long, filled with glass helices (3 mm I.D.) (Fig. 1).

6.5. Technicon proportioning pump fitted with 8 pumping tubes, 2.8 mm I.D.

6.6. A 100-mL graduated cylinder mounted with clamp on a retort stand so that its position can be adjusted.

6.7. Spectrophotometer for use at 620 nm, providing a light path of 1 cm.

7. Reagents

7.1. Sodium hydroxide solution, 1 N: Dissolve 50 g sodium hydroxide, NaOH, in 1 L distilled water.

7.2. Mercuric chloride solution: Dissolve 34 g mercuric chloride, $HgCl_2$, in 500 mL distilled water. **(Caution: Toxic; take care to avoid ingestion.)**

7.3. Magnesium chloride solution: Dissolve 51 g magnesium chloride, $MgCl_2 \cdot 6H_2O$, in 100 mL distilled water.

7.4. Sulphuric acid, H_2SO_4, concentrated.

7.5. Sodium hydroxide solution, 0.2 N: Dissolve 8 g sodium hydroxide, NaOH, in 1 L distilled water.

7.6. Acetic acid, CH_3COOH, conc. and 1 + 4.

7.7. Stock cyanide solution: Dissolve 2.51 g potassium cyanide, KCN, in 1 L water. Standardize with 0.0192 N silver nitrate, $AgNO_3$. The solution loses strength gradually and must be rechecked every week. Approximate strength, 1 mL = 1 mg CN. **(Caution: Toxic; take care to avoid ingestion.)**

7.8. Standard cyanide solution: Dilute 10 mL stock cyanide solution to 1 L with distilled water; mix and make a second dilution of 10 mL to 100 mL. 1.00 mL = 1.0 μg CN. This solution must be prepared daily. **(Caution: Toxic; take care to avoid ingestion.)**

7.9. Chloramine-T solution: Dissolve 1 g of chloramine-T, $CH_3C_6H_4SO_2NClNa \cdot 3H_2O$, in 100 mL water. Prepare daily.

7.10. 1-Phenyl-3-methyl-5-pyrazolone solution: Prepare a saturated aqueous solution (approximately 0.5 g/100 mL) by adding the pyrazolone, $C_{10}H_{10}N_2O$, to water at approximately 75°C. Agitate occasionally as the solution cools to room temperature. If necessary, the pyrazolone (melting point 127°C to 128°C) can be purified by recrystallization from ethyl alcohol. Usually this is not required.

7.11. Pyridine, C_5H_5N.

7.12. Bis-pyrazolone (3,3'-dimethyl-1,1'-diphenyl-$\left\{4,4'\text{-bi-2 pyrazoline}\right\}$-5,5' dione).

7.13. Mixed pyridine-pyrazolone reagent: Mix 125 mL of the filtered, saturated aqueous solution of pyrazolone with a filtered solution containing 0.025 g bis-pyrazolone dissolved in 25 mL pyridine. Several minutes of mixing is usually necessary to dissolve the bis-pyrazolone in pyridine. The mixed reagent develops a pink colour on standing, but if used within 24 h this does not affect the colour production with cyanide. Prepare daily.

7.14. Standard silver nitrate solution: Dissolve 3.27 g of silver nitrate, $AgNO_3$, in 1 L of distilled water. Store in a dark bottle. One millilitre of this solution is equivalent to 1.00 mg CN.

8. Procedure

8.1. Procedure for distillation.

8.1.1. Close pinch clamp (Fig. 1).

8.1.2. Add about 80 mL of water to the graduated cylinder and adjust the position of the cylinder so that the tube dips near the bottom of the cylinder.

8.1.3. Add 750 mL sample to the flask; insert stirring bar, and start the stirrer.

8.1.4. Add 50 mL 1 N NaOH solution (7.1) to the 250-mL beaker and start the pump.

8.1.5. When the absorption column is wet with NaOH solution, add 20 mL mercuric chloride solution (7.2) and 10 mL magnesium chloride solution (7.3) through the thistle tube.

8.1.6. Slowly add 37 mL concentrated sulphuric acid to the flask through the thistle tube.

8.1.7. Turn on the heating mantle and allow the contents of the flask to boil vigorously (Excess air as the flask heats up will escape from the equipment through the dip tube in the graduated cylinder).

8.1.8. After 1 h of boiling turn off the heating mantle and open pinch clamp.

8.1.9. Remove the tube pumping NaOH from the NaOH solution; rinse the contents of the column into the NaOH beaker by pumping approximately 150 mL distilled water through the absorption column and collect in the NaOH beaker.

8.1.10. Transfer quantitatively to a 250-mL volumetric flask and make up to the mark.

8.2. Procedure for colorimetric measurement.

8.2.1. Transfer 15 mL of distillate to a 50-mL beaker.

8.2.2. To prepare standard solutions for the calibration curve, use cyanide standard 1 mL = 1 μg CN. Pipette 0 (blank), 0.2 mL, 0.5 mL, 0.8 mL and 1.0 mL into 50-mL beakers and make up to 15 mL with NaOH, 0.2 N (7.5). Proceed with 8.2.3, treating samples and standards in the same manner.

8.2.3. Adjust pH to 6-7 with 1 + 4 acetic acid. Transfer to 25-mL volumetric flask.

8.2.4. Add 0.2 mL chloramine-T solution (7.9) and mix. Allow 1-2 min for the reaction.

8.2.5. Add 5.0 mL mixed pyridine-pyrazolone reagent (7.13) and make up to the mark; mix. Allow 20 min for colour development.

8.2.6. Read absorbance at 620 nm in a 1-cm cell.

8.2.7. As a check on the distillation step, periodically process cyanide standard solutions through the complete procedure.

9. Calculations

9.1. Prepare a calibration curve derived from the peak heights obtained with the standard solutions.

9.2. Determine the micrograms of cyanide in the samples by comparing sample peak heights with the calibration graph.

9.3. Calculate the cyanide concentration as follows:

$$\text{mg/L CN} = \frac{F \times D}{C \times E}$$

where E = cyanide determined (μg),
D = diluted absorbing solution (mL),
C = original sample (mL), and
E = aliquot used (mL).

10. Precision and Accuracy

10.1. No data available.

11. References

11.1. Goulden, P.D. Unpublished information on distillation setup. Water Quality Branch, Ottawa.

11.2. American Society for Testing and Materials. 1976. *Book of ASTM Standards.* Part 31. Water, pp. 503-505. Philadelphia.

11.3. American Public Health Association. 1975. *Standard Methods for the Examination of Water and Wastewater.* 14th ed. Washington, D.C.

11.4. Epstein, J. 1947. *Anal. Chem.* 19(4):272-274.

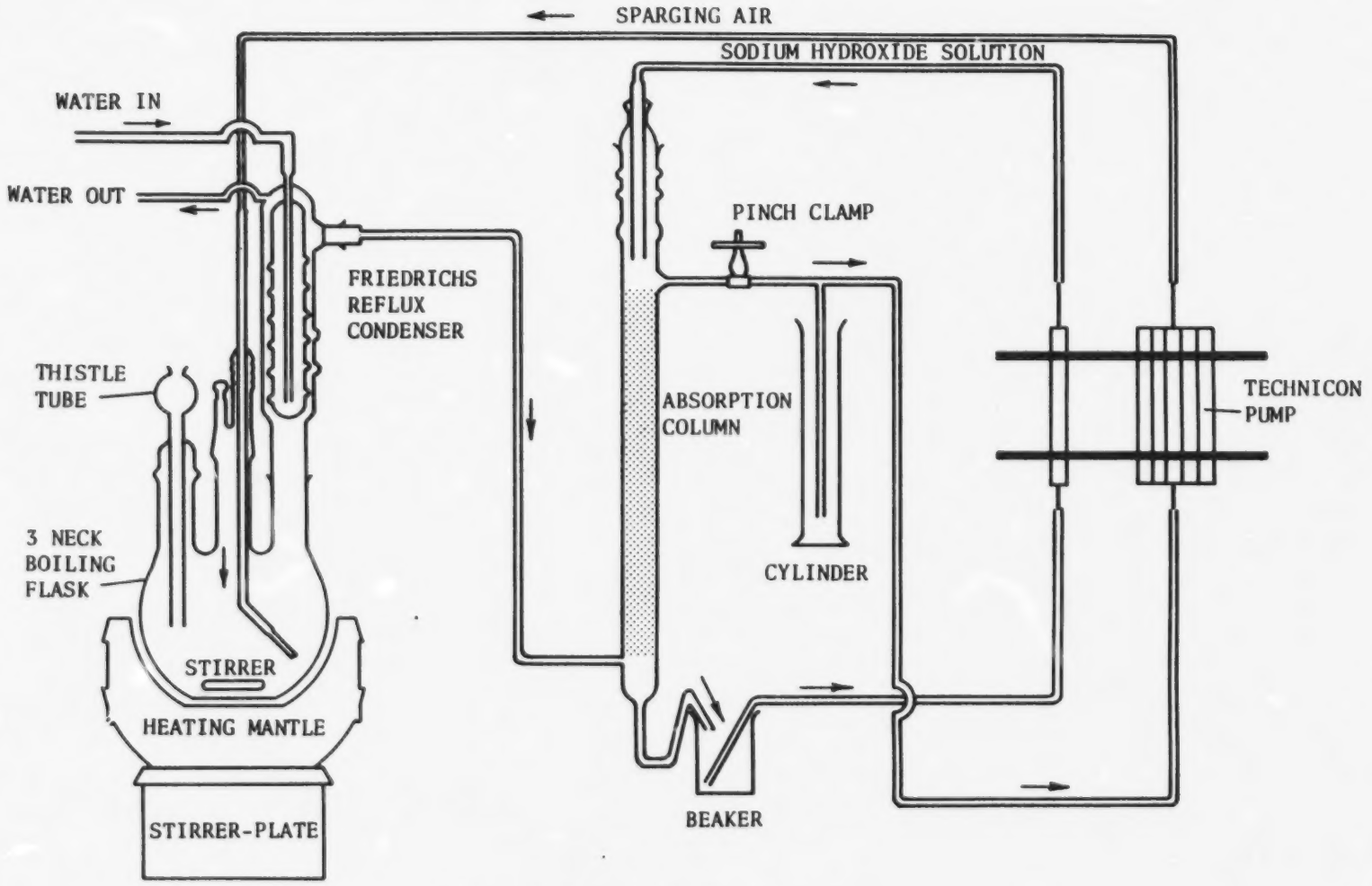


Figure 1. Cyanide distillation apparatus

NOVEMBER 1978

NAQUADAT No. 06604

CYANIDE

(Automated Pyridine-Pyrazolone)

1. Scope and Application

1.1. This method is applicable to the determination of cyanide in water and wastewaters in the range from 0.001 mg/L to 0.100 mg/L HCN.

1.2. The detection limit for this method is 0.001 mg/L CN^-.

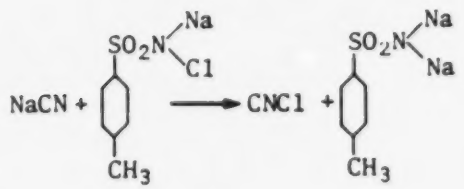
2. Principle and Theory

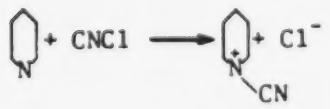
2.1. Complex cyanides are converted to hydrocyanic acid, HCN, by irradiation with ultraviolet light. After irradiation the sample is distilled from phosphoric acid solution into a sodium acetate absorbing solution.

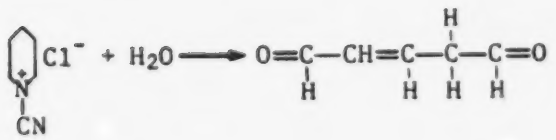
2.2. In the colorimetric measurement, the cyanide in sodium acetate solution is converted to cyanogen chloride, CNCl, by reaction with chloramine-T. The CNCl then forms a blue dye on the addition of pyridine-pyrazolone reagent, and the absorbance is measured at 620 nm.

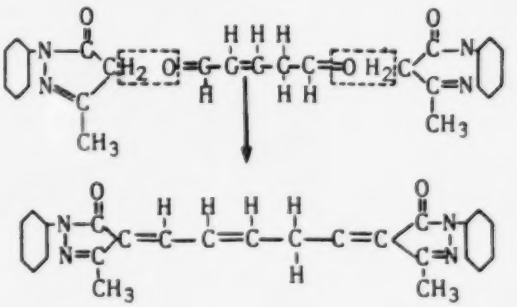
2.3. Equations:

The reaction may be expressed by the following equations (ref. 11.3):









3. Interferences

3.1. Sulphides interfere and should be removed prior to analysis (see section 5).

3.2. Thiocyanate gives an apparent total cyanide on an equimolar basis.

3.3. Some organic cyanide compounds such as nitriles are decomposed under test conditions.

3.4. Other interfering substances are removed in the distillation step.

4. Sampling Procedure and Storage

4.1. The sample should be collected in a 125-mL plastic bottle and analyzed as soon as possible after collection.

4.2. Samples should be preserved by addition of sufficient NaOH to raise the pH to 11. Usually 1 mL of 10% sodium hydroxide solution per 100-mL sample is adequate.

5. Sample Preparation

5.1. If sulphide is present, decant a 100-mL aliquot of sample and add 0.5 g citric acid and 0.5 g sodium bisulphite, $NaHSO_3$. Stir the solution and allow to stand for 15 min. Decant the supernatant from the precipitated sulphur and neutralize the excess sulphite with hydrogen peroxide (30%), using starch-iodide paper as an indicator. Then immediately treat the sample aliquot with sodium hydroxide solution to raise the pH to above 10.

5.2. Treat samples containing free chlorine with sodium bisulphite using starch-iodide paper as an indicator.

6. Apparatus

6.1. Technicon AutoAnalyzer unit consisting of:

6.1.1. Manifold (Fig. 1).

6.1.2. Recorder.

6.1.3. Sampler.

6.1.4. Colorimeter equipped with 50-mm flow cell and 620-nm filters.

6.2. Proportioning pump, Carlo-Erba model 1512/20.

6.3. UV reactor. The coil consists of quartz tubing, 3 mm I.D. and 12 m long, wound to a diameter of 13 cm. A 400-W mercury lamp is used. For description of the reactor, see the "Nitrogen: Organic" (automated ultraviolet digestion) method.

6.4. Distillation equipment (see Fig. 2). The distillation column consists of borosilicate glass tubing, 12 mm I.D. and 350 mm long, wrapped with 22-gauge heating wire to give a resistance of about 24 ohms. Approximately 65 V ac is applied to the heating wire using a variable transformer.

6.5. Gas absorption column. For details of construction, see Figure 3.

7. Reagents

7.1. Stock cyanide solution, 1000 mg/L as CN: Dissolve 2.51 g potassium cyanide, KCN, in distilled water. Add 10 mL of 10% sodium hydroxide solution (7.2) and make up to 1 L in a volumetric flask. Standardize with 0.0192 N silver nitrate solution using indicator solution (7.4). The solution gradually loses strength and must be rechecked every 2 weeks. **(Caution: Toxic; take care to avoid ingestion.)**

7.2. Sodium hydroxide solution, 10%: Dissolve 100 g sodium hydroxide, NaOH, in approximately 750 mL distilled water and make up to 1 L.

7.3. Standard silver nitrate solution, 0.0192 N: Dissolve 3.270 g silver nitrate, $AgNO_3$, in distilled water and dilute to 1 L in a volumetric flask (1 mL of this solution is equivalent to 1 mg CN).

7.4. Indicator solution: Dissolve 0.02 g rhodanine (p-dimethylaminobenzylidene) in 100 mL acetone.

7.5. Intermediate cyanide solution, 10 mg/L as CN: Dilute 10 mL stock cyanide solution (7.1) and 10 mL sodium hydroxide solution (7.2) to 1 L with distilled water.

7.6. Standard cyanide solution, 0.1 mg/L as CN: Dilute 10 mL intermediate cyanide solution (7.5) and 10 mL sodium hydroxide solution (7.2) to 1 L with distilled water.

7.7. Working cyanide standards: Prepare a series of standards to cover the required concentration range by appropriate dilutions of the standard cyanide solution (7.6). All standards should be preserved with sodium hydroxide solution at the rate of 1 mL of 10% NaOH per 100 mL solution.

7.8. Phosphoric acid solution: Dilute reagent grade o-phosphoric acid, H_3PO_4, with an equal volume of distilled water.

7.9. Hypophosphorous acid solution: Dilute 50% hypophosphorous acid, $H(H_2PO_2)$, with an equal volume of distilled water.

7.10. Sodium acetate solution, 2%: Dissolve 20 g sodium acetate, CH_3COONa, in distilled water and make up to 1 L. Adjust the pH of this solution to 6.5 with acetic acid (glacial).

7.11. Wash solution, 0.1% sodium hydroxide solution: Dilute 20 mL of 10% sodium hydroxide solution (7.2) to 2 L with distilled water.

7.12. Mixed pyridine-pyrazolone solution: Dissolve 0.75 g 3-methyl-1-phenyl-2-pyrazolin-5-one and 0.05 g 3,3′-dimethyl-1,1′-diphenyl-(4,4′-bi-2-pyrazoline)-5,5′-dione in 50 mL pyridine. Add 250 mL distilled water and mix. Prepare daily.

7.13. Chloramine-T solution: Dissolve 1 g chloramine-T, $CH_3C_6H_4SO_2NClNa \cdot 3H_2O$, in 100 mL distilled water. Prepare daily.

8. Procedure

8.1. Set the system in operation and allow to warm up.

8.2. Determine the rate of distillation by measuring the volume of liquid that overflows from each of the two U-tube traps. Adjust the power to the distillation column heater so that approximately 20% of the liquid is being vaporized in the tube.

8.3. Check to see that the conical joint at the top of the gas absorber column is filled with sodium acetate solution.

8.4. Run sodium hydroxide-treated standards and samples at 20 per hour.

9. Calculations

9.1. Prepare a calibration curve from the peak heights obtained with the standard solutions.

9.2. Determine the concentration of cyanide in the samples by comparing sample peak heights with the calibration curve.

10. Precision and Accuracy

10.1. In a single laboratory (Water Quality Branch), a natural water sample was analyzed and the coefficient of variation at a level of 0.023 mg/L was ±3.8%. The same sample was spiked with 0.025 mg/L cyanide and the mean concentration found was 0.046 mg/L with a coefficient of variation of ±2.2%. The average percent recovery was 94%.

10.2. The recoveries of standard solutions of complex cyanides were compared with the recoveries of simple cyanide standard solutions (KCN).

Complex cyanide	Recovery (%)
Potassium hexacyanocobaltate	78–80
Potassium tetracyanonickelate	75–80
Potassium ferrocyanide	95–100
Potassium ferricyanide	95–100

11. References

11.1. Goulden, P. D., B. K. Afghan and P. Brooksbank. 1972. Determination of nanogram quantities of simple and complex cyanides in water. *Anal. Chem.* 44:1845-1849.

11.2. American Public Health Association. 1971. *Standard Methods for the Examination of Water and Wastewater.* 13th ed. Washington, D.C.

11.3. Epstein, J. 1947. *Anal. Chem.* 19(4):272-274.

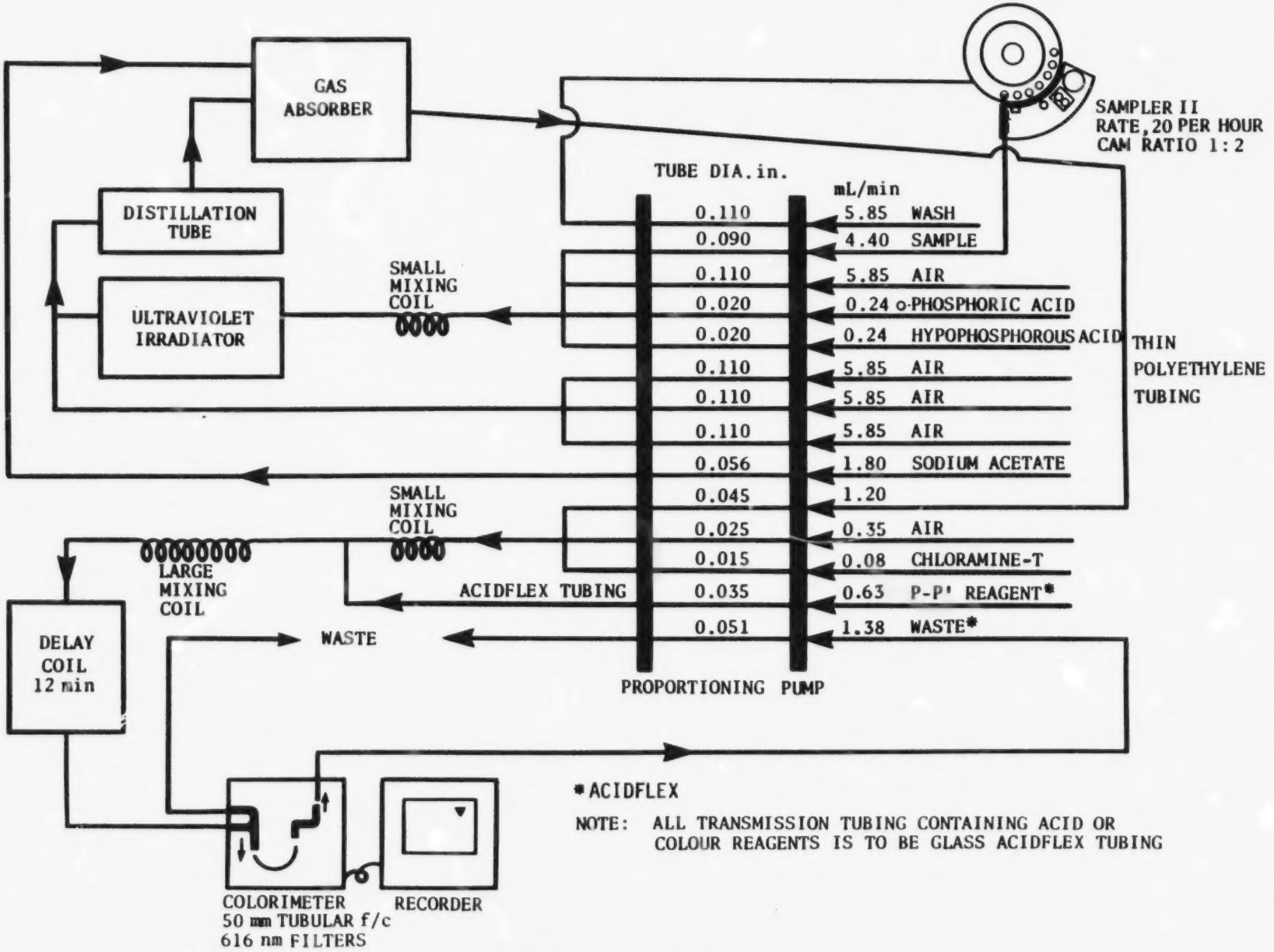


Figure 1. Cyanide manifold

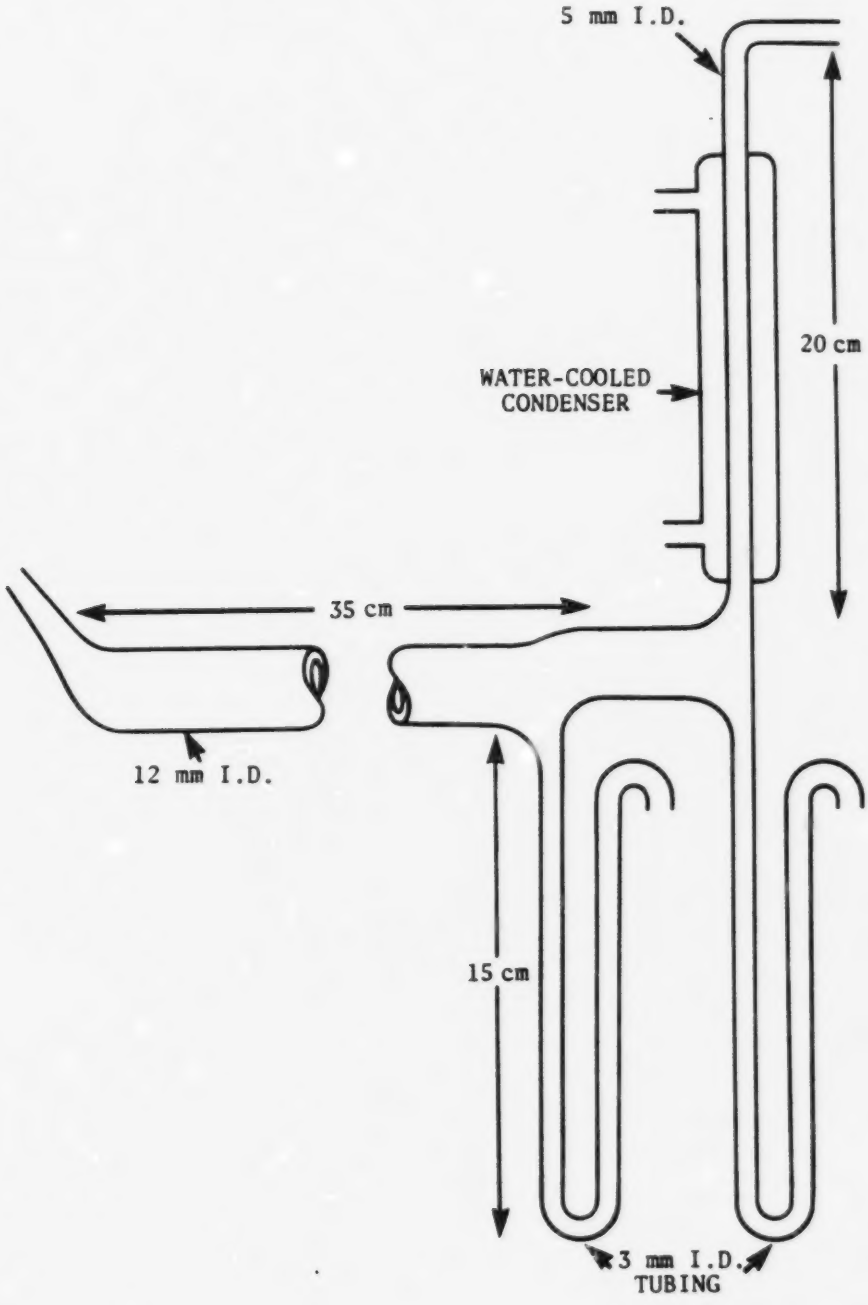


Figure 2. Continuous distillation apparatus

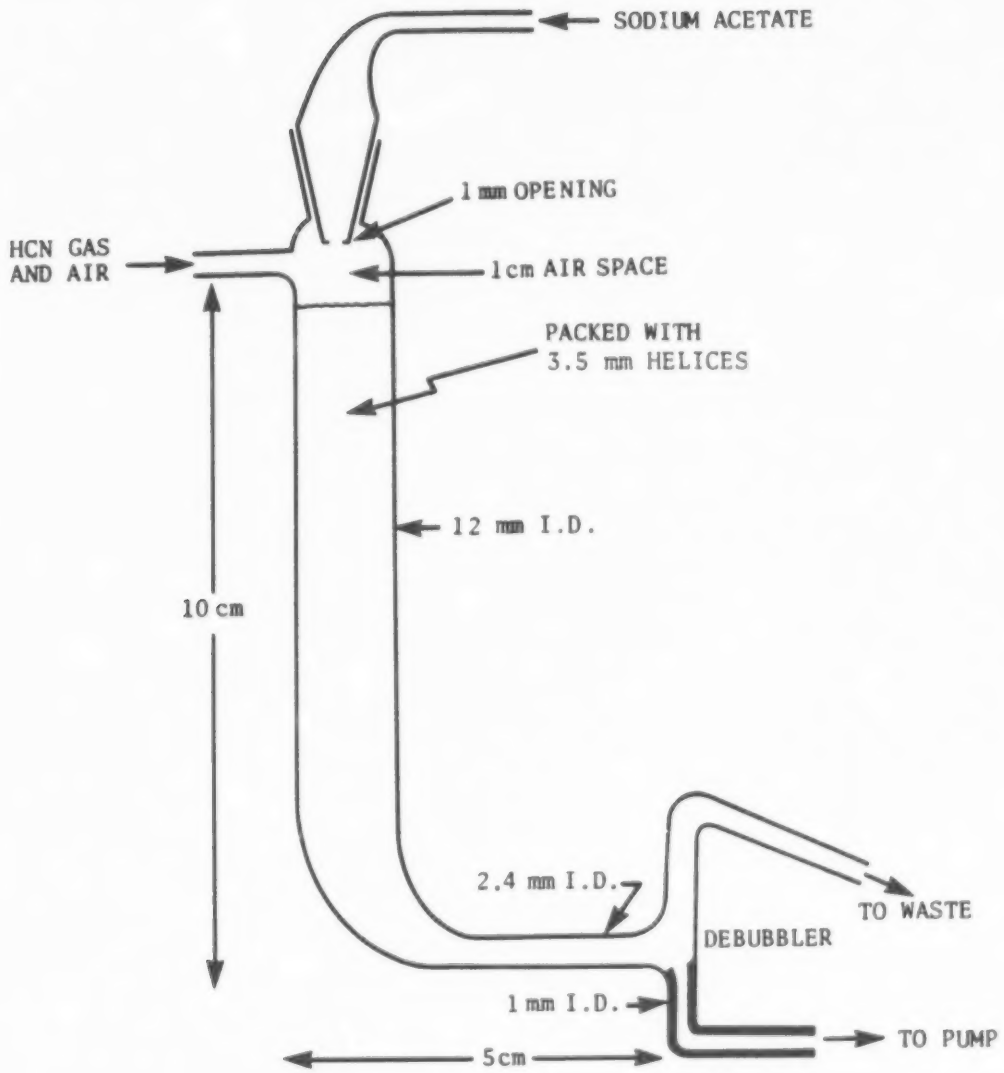


Figure 3. Gas absorption column

APPENDIX C

ANALYTICAL RESULTS

Appendix C

Parameter (mg/l)	Barren	Acidified
pH (20'C)	10.94	2.00
Conductivity (mmho)	3.37	5.32
TDS	2700	3000
TOC	450	270
Fluoride	< 0.05	2.7
Chloride	160	139
Nitrite as N	6.5	< 0.2
Bromide	< 0.40	< 0.8
Nitrate as N	3.0	4.1
Phosphate as P	< 0.40	< 0.8
Sulfate	400	1950
Alkalinity	2060	< 1
Cyanide	660	450
Thiocyanate	320	320
Calcium	101	93
Magnesium	0.30	0.35
Sodium	590	470
Potassium	50	13
Aluminum	0.99	1.0
Barium	0.009	0.19
Beryllium	< 0.0003	< 0.0003
Boron	0.69	0.59
Cadmium	< 0.002	< 0.002
Chromium	< 0.004	< 0.004
Cobalt	1.5	< 0.01
Copper	46	5.4
Iron	18	0.58
Lead	< 0.04	< 0.04
Manganese	0.01	0.02
Molybdenum	0.13	0.11
Nickel	33	19
Phosphorous	0.21	< 0.10
Silicon	1.8	2.0
Silver	< 0.01	< 0.01
Strontium	0.32	0.29
Thallium	< 0.02	< 0.02
Titanium	< 0.01	< 0.01
Vanadium	< 0.02	< 0.02
Zinc	50	39
Zirconium	< 0.01	< 0.01

High pH Membrane Selection Test

Parameter (mg/l)	Feed	FT-30 Permeate	Desal - 1 Permeate	Toray Permeate
Conductivity (mmho)	2.52	0.970	0.764	0.329
pH (20°C)	10.37	10.25	10.80	10.83
Cyanide	760	240	150	50
Thiocyanate	130	49	37	4.8
Fluoride	11	3.4	0.25	0.28
Chloride	160	48	25	0.17
Nitrite as N	7.4	2.4	0.32	0.22
Bromide	< 0.80	< 0.80	< 0.80	< 0.08
Nitrate as N	2.7	0.99	0.49	0.35
Phosphate as P	< 0.80	< 0.80	< 0.80	< 0.08
Sulfate	430	130	63	0.14
TOC	403	105	79	28
Calcium	66	21	10	0.09
Magnesium	0.37	0.13	0.05	< 0.05
Sodium	600	220	160	57
Potassium	45	16	10	4.7
Aluminum	1.1	0.35	0.28	< 0.03
Barium	0.05	0.02	0.007	< 0.002
Beryllium	< 0.0003	< 0.0003	< 0.0003	< 0.0003
Boron	0.70	0.19	0.13	< 0.01
Cadmium	< 0.002	< 0.002	< 0.002	< 0.002
Chromium	< 0.004	< 0.004	< 0.004	< 0.004
Cobalt	1.5	0.48	0.23	< 0.01
Copper	48	15	7.1	< 0.006
Iron	18	5.9	2.7	< 0.01
Lead	< 0.04	< 0.04	< 0.04	< 0.04
Manganese	< 0.005	< 0.005	< 0.005	< 0.005
Molybdenum	0.14	0.04	< 0.02	< 0.02
Nickel	34	11	5.0	< 0.009
Phosphorous	< 0.10	< 0.10	< 0.10	< 0.10
Silicon	2.3	0.75	0.43	< 0.05
Silver	< 0.01	< 0.01	< 0.01	< 0.01
Strontium	0.26	0.08	0.04	< 0.001
Thallium	< 0.02	< 0.02	< 0.02	< 0.02
Titanium	< 0.01	< 0.01	< 0.01	< 0.01
Vanadium	< 0.02	< 0.02	< 0.02	< 0.02
Zinc	51	16	7.6	0.02
Zirconium	< 0.01	< 0.01	< 0.01	< 0.01

Low pH Membrane Selection Test

Parameter (mg/l)	Feed	FT-30 Permeate	Desal - 2 Permeate	Toray Permeate
Conductivity (mmho)	4.40	1.51	0.478	0.048
pH (20'C)	2.16	2.70	3.68	5.69
Cyanide	340	265	250	220
Thiocyanate	130	54	15	7.5
Fluoride	2.2	2.1	1.3	< 0.01
Chloride	110	32	9.0	1.0
Nitrite as N	< 2.0	< 0.40	0.19	0.37
Bromide	< 8.0	< 1.6	< 0.80	< 0.08
Nitrate as N	2.5	0.94	0.38	0.10
Phosphate as P	< 8.0	< 1.6	< 0.80	< 0.08
Sulfate	1400	460	130	0.95
TOC	240	186	175	150
Calcium	100	29	8.6	0.12
Magnesium	2.6	0.73	0.21	< 0.05
Sodium	520	170	63	8.6
Potassium	36	11	4.3	< 0.4
Aluminum	4.3	1.3	0.37	< 0.03
Barium	0.09	0.02	0.008	< 0.002
Beryllium	< 0.0003	< 0.0003	< 0.0003	< 0.0003
Boron	0.56	0.18	0.40	0.21
Cadmium	< 0.002	< 0.002	< 0.002	< 0.002
Chromium	0.01	< 0.004	< 0.004	< 0.004
Cobalt	0.03	< 0.01	< 0.01	< 0.01
Copper	5.7	1.7	0.58	0.26
Iron	1.1	0.88	0.09	< 0.01
Lead	< 0.04	< 0.04	< 0.04	< 0.04
Manganese	0.04	0.01	< 0.005	0.02
Molybdenum	0.11	0.04	< 0.02	< 0.02
Nickel	19	5.5	1.7	< 0.009
Phosphorous	< 0.10	< 0.10	< 0.10	< 0.10
Silicon	4.3	1.2	1.1	0.11
Silver	< 0.01	< 0.01	< 0.01	< 0.01
Strontium	0.36	0.10	0.03	< 0.001
Thallium	< 0.02	< 0.02	< 0.02	< 0.02
Titanium	< 0.01	< 0.01	< 0.01	< 0.01
Vanadium	< 0.02	< 0.02	< 0.02	< 0.02
Zinc	38	9.9	3.1	0.007
Zirconium	< 0.01	< 0.01	< 0.01	< 0.01

High pH Concentration Tests

Parameter (mg/l)	CF = 2.5		CF = 5		CF = 10	
	Feed	Permeate	Feed	Permeate	Feed	Permeate
Conductivity (mmho)	6.11	0.510	9.67	0.907	14.22	1.578
pH (20'C)	10.09	10.53	10.00	10.45	9.82	10.42
Cyanide	1730	96	2460	200	3700	370
Thiocyanate	450	5.4	600	7.1	1100	12
Fluoride	-	-	-	-	67	2.0
Chloride	-	-	-	-	1100	6.5
Nitrite as N	-	-	-	-	47	1.6
Bromide	-	-	-	-	6.9	1.5
Nitrate as N	-	-	-	-	12	< 2.0
Phosphate as P	-	-	-	-	< 8.0	< 0.80
Sulfate	-	-	-	-	3000	1.5
TOC	890	56	1170	97	1810	230
Calcium	-	-	-	-	230	4.1
Magnesium	-	-	-	-	3.7	0.18
Sodium	-	-	-	-	5020	330
Potassium	-	-	-	-	220	22
Aluminum	-	-	-	-	0.24	< 0.03
Barium	-	-	-	-	0.05	0.02
Beryllium	-	-	-	-	< 0.0003	< 0.0003
Boron	-	-	-	-	4.5	0.19
Cadmium	-	-	-	-	< 0.002	< 0.002
Chromium	-	-	-	-	< 0.004	< 0.004
Cobalt	-	-	-	-	9.8	< 0.01
Copper	-	-	-	-	340	0.18
Iron	-	-	-	-	120	0.07
Lead	-	-	-	-	< 0.04	< 0.04
Manganese	-	-	-	-	< 0.005	< 0.005
Molybdenum	-	-	-	-	0.93	< 0.02
Nickel	-	-	-	-	220	0.14
Phosphorous	-	-	-	-	< 0.10	< 0.10
Silicon	-	-	-	-	7.4	0.10
Silver	-	-	-	-	< 0.01	< 0.01
Strontium	-	-	-	-	1.3	0.03
Thallium	-	-	-	-	< 0.02	< 0.02
Titanium	-	-	-	-	< 0.01	< 0.01
Vanadium	-	-	-	-	< 0.02	< 0.02
Zinc	-	-	-	-	260	0.22
Zirconium	-	-	-	-	< 0.01	< 0.01

Low pH Concentration Tests

Parameter (mg/l)	CF = 2.5		CF = 5.0		CF = 10.0	
	Feed	Permeate	Feed	Permeate	Feed	Permeate
Conductivity (mmho)	9.80	0.135	16.22	0.278	23.94	0.459
pH (20'C)	2.19	4.11	1.96	4.04	1.89	3.49
Cyanide	290	250	600	250	970	290
Thiocyanate	420	24	790	54	950	150
Fluoride	-	-	< 1.0	2.9	11	1.6
Chloride	-	-	480	17	960	32
Nitrite as N	-	-	< 2.0	0.16	< 2.0	< 0.20
Bromide	-	-	36	4.1	< 8.0	< 0.80
Nitrate as N	-	-	< 2.0	< 0.20	18	2.3
Phosphate as P	-	-	< 8.0	< 0.80	< 8.0	< 0.80
Sulfate	-	-	6200	6.0	12000	11
TOC	310	210	420	200	730	230
Calcium	-	-	390	6.1	360	0.49
Magnesium	-	-	4.0	0.78	6.1	< 0.05
Sodium	-	-	1490	43	5200	93
Potassium	-	-	100	2.6	120	5.0
Aluminum	-	-	8.9	< 0.03	9.8	< 0.03
Barium	-	-	0.20	0.005	0.11	< 0.002
Beryllium	-	-	< 0.0003	< 0.0003	< 0.0003	< 0.0003
Boron	-	-	1.1	0.65	1.3	0.85
Cadmium	-	-	0.02	< 0.002	0.04	< 0.002
Chromium	-	-	0.04	< 0.004	0.06	< 0.004
Cobalt	-	-	0.13	< 0.01	0.19	< 0.01
Copper	-	-	17	0.16	25	0.11
Iron	-	-	3.1	0.01	4.5	< 0.01
Lead	-	-	0.37	< 0.04	0.59	< 0.04
Manganese	-	-	0.10	< 0.005	0.16	< 0.005
Molybdenum	-	-	0.40	< 0.02	0.56	< 0.02
Nickel	-	-	67	0.03	130	0.08
Phosphorous	-	-	0.64	< 0.10	1.3	< 0.10
Silicon	-	-	11	0.66	17	0.99
Silver	-	-	< 0.01	< 0.01	< 0.01	< 0.01
Strontium	-	-	1.0	0.03	1.0	0.002
Thallium	-	-	< 0.02	< 0.02	< 0.02	< 0.02
Titanium	-	-	< 0.01	< 0.01	< 0.01	< 0.01
Vanadium	-	-	< 0.02	< 0.02	< 0.02	: 0.02
Zinc	-	-	130	0.09	220	0.14
Zirconium	-	-	< 0.01	< 0.01	< 0.01	< 0.01

APPENDIX D

RESULTS OF MEMBRANE QUALIFICATION TEST

Appendix D

Summary of Salt Flux Runs

salt flux run #	Membrane FT-30 Flux (usgfd)	% Rejection	Membrane Desal-1 Flux (usgfd)	% Rejection	Membrane Toray Flux (usgfd)	% Rejection
1	25.35	99.3	55.17	94.88	15.69	99.63
2	33.8	85.49	57.07	94.3	16.6	99.2
			Membrane Desal-2			
3	25.35	99.59	32.29	96.66	17.6	99.29
4	33.8	99.45	30.44	96.81	19.02	99.63
5					21.4	99.49
6					22.3	99.53

APPENDIX E

SCALING CALCULATIONS

INPUT DATA FOR SCALE CALCULATIONS

	Barren Bleed	CONC.
Concentration		1
Temperature (C)	20	
pH	10.94	10.94
Electrical Conductance (uS/cm)		
TDS (mg/l)	2700	2700
Silica (as SiO2)(mg/l)		0
Aluminum (mg/l)	0	0
Barium	0	0
Cadmium	0	0
Calcium	101	101
Iron	18	18
Magnesium	0.3	0.3
Manganese	0	0
Potassium	50	50
Sodium	590	590
Strontium	0	0
Zinc	50	50
Alkalinity (as CaCO3)	790	790
Bromide (mg/l)	0	0
Chloride	160	160
Fluoride	0	0
Nitrate (as N)	0	0
Nitrite (as N)	0	0
Phosphate (as P)	0	0
Sulfate	400	400

Sum of Cations	**34.57**		**Iron Level is High**
Sum of Anions	**-28.63**		
Charge Balance(%)	**17%**		
LANGELIER SATURATION INDEX		**1.43**	'+' = CaCO3 fouling potential '-' = no CaCO3 fouling
SATURATION pH 12.37			
lb HCl/1000 gal to adjust =	**0.00**		
RELATIVE SATURATIONS	CaSO4 =	**0.05**	
	BaSO4 =	**0.00**	> 1 suggests scale formation potential
	SrSO4 =	**0.00**	
RELATIVE SILICA SATURATION		**#DIV/0!**	
OSMOTIC PRESSURE		**12**	**psi**

INPUT DATA FOR SCALE CALCULATIONS

	Barren Bleed	CONC.
Concentration		10
Temperature (C)	20	
pH	10.94	10.94
Electrical Conductance (uS/cm)		
TDS (mg/l)	2700	27000
Silica (as SiO2)(mg/l)		0
Aluminum (mg/l)	0	0
Barium	0	0
Cadmium	0	0
Calcium	101	1010
Iron	18	180
Magnesium	0.3	3
Manganese	0	0
Potassium	50	500
Sodium	590	5900
Strontium	0	0
Zinc	50	500
Alkalinity (as CaCO3)	790	7900
Bromide (mg/l)	0	0
Chloride	160	1600
Fluoride	0	0
Nitrate (as N)	0	0
Nitrite (as N)	0	0
Phosphate (as P)	0	0
Sulfate	400	4000

Sum of Cations	**345.75**		**Iron Level is High**
Sum of Anions	**-286.31**		
Charge Balance(%)	**17%**		
LANGELIER SATURATION INDEX		**2.43**	'+' = CaCO3 fouling potential
SATURATION pH 13.37			'-' = no CaCO3 fouling
lb HCl/1000 gal to adjust =	**0.00**		
RELATIVE SATURATIONS	CaSO4 =	**1.21**	
	BaSO4 =	**0.00**	> 1 suggests scale formation
	SrSO4 =	**0.00**	potential
RELATIVE SILICA SATURATION		**#DIV/0!**	
OSMOTIC PRESSURE		**121**	**psi**

INPUT DATA FOR SCALE CALCULATIONS

	Barren Bleed	CONC.
Concentration		20
Temperature (C)	20	
pH	10.94	10.94
Electrical Conductance (uS/cm)		
TDS (mg/l)	2700	54000
Silica (as SiO2)(mg/l)		0
Aluminum (mg/l)	0	0
Barium	0	0
Cadmium	0	0
Calcium	101	2020
Iron	18	360
Magnesium	0.3	6
Manganese	0	0
Potassium	50	1000
Sodium	590	11800
Strontium	0	0
Zinc	50	1000
Alkalinity (as CaCO3)	790	15800
Bromide (mg/l)	0	0
Chloride	160	3200
Fluoride	0	0
Nitrate (as N)	0	0
Nitrite (as N)	0	0
Phosphate (as P)	0	0
Sulfate	400	8000

Sum of Cations	**691.49**		**Iron Level is High**
Sum of Anions	**-572.61**		
Charge Balance(%)	**17%**		
LANGELIER SATURATION INDEX		**2.73**	'+' = CaCO3 fouling potential '-' = no CaCO3 fouling
SATURATION pH	**13.67**		
lb HCl/1000 gal to adjust =	**0.00**		
RELATIVE SATURATIONS	CaSO4 =	**2.93**	
	BaSO4 =	**0.00**	> 1 suggests scale formation potential
	SrSO4 =	**0.00**	
RELATIVE SILICA SATURATION		**#DIV/0!**	
OSMOTIC PRESSURE		**242**	**psi**

Sulfuric Acid Equilibrium

$$H_2SO_4 \xrightarrow{\text{strong}} H^+ + HSO_4$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

$$K_2 = 0.012 = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$$

$$\frac{[SO_4^{2-}]}{[HSO_4^-]} = \frac{0.012}{[H^+]} = \frac{0.012}{0.010} = \frac{1.2}{1}$$

pH 2 $\quad pH = -\log [H^+] = 2$

$$\log [H^+] = -2$$

$$[H^+] = 10^{-2}\ M = 0.01\ M$$

$\therefore$ at pH 2 ; the distribution is SO_4^{2-} 55%

HSO_4^- 45%